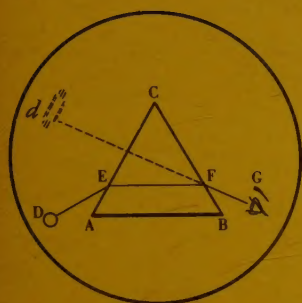




UNIVERSITY OF ILLINOIS
LIBRARY

AUG 4 1961

CHICAGO

optics and spectroscopy

volume x
number 4
april 1961

OPTICAL SOCIETY OF AMERICA

USSR ACADEMY OF SCIENCES

RUSSIAN EDITORIAL STAFF FOR
OPTIKA I SPEKTROSKOPIYA sponsored by
USSR ACADEMY OF SCIENCES

Editor: S. E. FRISH

Assistant Editor: P. P. FEOFILOV

Corresponding Secretary: L. S. SAZONOV

Associate Editors:

M. M. GUREVICH M. A. EL'IASHEVICH A. A. LEBEDEV V. P. LINNIK
S. L. MANDEL'SHTAM I. V. OBREIMOV V. K. PROKOF'EV
N. N. SOBOLEV A. N. TERENIN A. I. TUDOROVSKII

Translated from *OPTIKA I SPEKTROSKOPIYA* on the initiative of THE OPTICAL SOCIETY OF AMERICA, INC. with a grant-in-aid from THE NATIONAL SCIENCE FOUNDATION. *Optics and Spectroscopy* is a cover-to-cover translation of *Optika i Spektroskopiya* and no attempt is made to edit the material other than to correct obvious misprints. The views are those of the original authors and do not represent the Optical Society of America.

TRANSLATION EDITORIAL STAFF

Scientific Editors

CYRUS FELDMAN, *Oak Ridge National Laboratory*

CARL W. GARLAND, *Massachusetts Institute of Technology*

MATHEW G. GIBBONS, *Oakland, California*

Administrative Editor:

PATRICIA R. WAKELING, *OSA*

Published monthly by the Optical Society of America, Inc. Executive office: 1155 Sixteenth Street, N.W., Washington, D.C. Subscriptions for one year to members of the Society: Associates \$13.00; Regular members and Fellows \$17.00. Subscriptions for non-members of the Society: One year U. S. and Possessions, \$25.00; Foreign \$28.00. Back numbers: \$3.00 per copy. Subscriptions, changes of address and undeliverable copies should be referred to the Executive offices in Washington, D.C. The office of publication is 2500 South State Street, Ann Arbor, Michigan. Second class postage paid at Ann Arbor, Michigan.

OSCILLATOR STRENGTHS OF THE SPECTRAL LINES OF CALCIUM

Yu. I. Ostrovskii and N. P. Penkin (pp. 429-435)

Received 23 May 1960

The relative f numbers of thirty-four CaI lines, situated between 2275 and 6572 Å are measured by the hook method. The results of the measurements are compared with the data of other authors.

INTRODUCTION

The relative oscillator strengths of the spectral lines of calcium have been measured by Prokof'ev,¹ Filippov and Kremnevskii,² Schuttevaer et al.,³ Allen,⁴ and Katz and Ornstein.⁵

In the first two papers, the relative f numbers of the absorption lines originating at the normal level (4^1S_0) of the calcium atom are measured by the hook method. Prokof'ev measured the ratio of the f numbers of the resonance ($4^1S_0-4^1P_1^0$) and intercombination ($4^1S_0-4^3P_1^0$) lines. It was found to be equal to 3.3×10^4 . Filippov and Kremnevskii found that the dependence of the oscillator strengths of the lines of the main series of singlets upon the main quantum number (n) has a clearly expressed maximum for the third member ($n = 6$). (We would like to point out that in their paper, the line $\lambda = 2721.65$ is incorrectly related to the second member of the main series. At the present time it is believed that it corresponds to the transition $4^1S_0-4p^1P_1$.)^{6,7}

Investigations³⁻⁵ which used the emission method, for the most part, measured the transition probabilities of the lines arising from transitions between excited states of the calcium atom. Most of the measurements were made for multiplets as a whole. The results of Allen and Schuttevaer show poor agreement. Thus at present there are no reliable experimental data on the oscillator strengths of the calcium lines just indicated. It is true that King and his associates⁸ have measured the relative numbers of a large number of calcium lines by the absorption method, but these results have not been published.

This situation has made it necessary for us to undertake the present investigation. Its goal is the determination of the oscillator strengths of the spectral lines of calcium by the hook method, which is the most reliable one.

EXPERIMENT

Spectrograms with hooks adjacent to the calcium lines were obtained with the aid of the interferometer arrangement described in refs. 9 and 10. In order to obtain well-defined hooks for the largest possible number of lines, and to express the relative f numbers of these lines on a common scale, the investigation was divided into three parts.

1. First, the oscillator strengths of the first three members of the main series of singlets and of the intercombination line 6572.8 Å ($4^1S_0-4^3P_1^0$) were measured. In this case, the column of calcium vapor was obtained in an evacuated quartz tube, about 1 meter long and 35 mm in diameter, placed in an electric resistance oven.¹¹ Metallic calcium was placed in a porcelain tube (1 =

60 cm) inserted into the quartz one. The porcelain tube protects the hot quartz ($t = 700-900^\circ\text{C}$) from interaction with the calcium vapor. In order to prevent the calcium vapor from condensing on the plane quartz end windows of the quartz tube, the latter was filled with several mm of helium or argon.

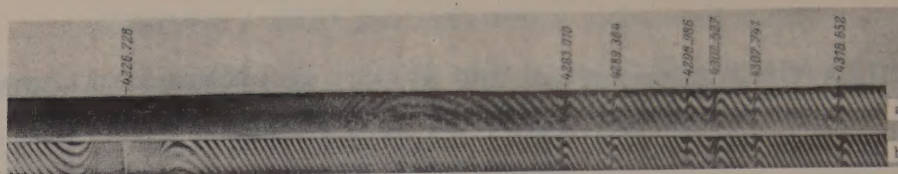
2. In order to photograph the hooks near the calcium lines originating at excited levels in a mixture consisting of inert gas and calcium vapor, a high frequency electric discharge was used. The quartz tube just described was provided with external electrodes, which were connected to a high-frequency oscillator made by the model shop of the Scientific Research Institute of Physics, Leningrad State University.

Upon initiation of the discharge, well-defined hooks appeared near the lines of the first three members of the diffuse series ($4^3P_{0,1,2}^0-n^3D_{1,2,3}$; $n = 4, 5, 6$), the two first members of the sharp series ($4^3P_{0,1,2}^0-n^3S_1$; $n = 5, 6$), and the multiplets $4^3P_{0,1,2}^0-4p^2^3P_{0,1,2}$ and $3^3D_{1,2,3}-4^3F_{2,3,4}$ of calcium.

3. If a high frequency, low pressure discharge is used to excite spectral lines, the f numbers of these lines cannot be expressed on one scale, since the relative population of the energy levels is unknown. In King's oven, as is known, quasi-equilibrium conditions exist;^{12,13} this permits the application of Boltzmann's formula for the computation of the distribution of atoms among energy levels. The third stage of our work therefore consisted of the following: Utilizing a King oven as our calcium vapor column, we measured the relative oscillator strengths of the spectral lines of the multiplet $4^3P_{0,1,2}^0-4p^2^3P_{0,1,2}$ and the resonance line $4^1S_0-4^1P_1^0$. This made it possible to refer all of the f numbers for transitions beginning at the $4^3P_{0,1,2}^0$ and 4^1S_0 levels to a single scale. In the King oven we were not able to obtain a sufficient population of level $3^3D_{1,2,3}$, so that we did not measure hooks near the lines beginning at this level.

Spectrograms were photographed at oven temperatures between 2600 and 2900°K. In order to decrease the errors connected with inhomogeneity of the temperature and density of the vapor column, the heated portion was made spindle-shaped,¹⁰ and the photographing of the hooks was conducted immediately after the oven was heated, while the metallic calcium had not yet migrated to the cool end of the tube.

The illustration shows photographs of hooks at the resonance line of calcium and the lines of the multiplet $4^3P_{0,1,2}^0-4p^2^3P_{0,1,2}$, photographed in a King oven (photo a) at 2800°K, and in a high frequency discharge (photo b). From comparison of pictures a and b it is seen that in order to obtain the same dispersion for the lines originating at the $4^3P_{0,1,2}^0$ level, a much smaller calcium atom concentration is required in a discharge than in a King



Photograph of hooks at the spectral lines of calcium. a—King oven, $T = 2500^\circ\text{K}$; b—high frequency discharge.

oven. This indicates that the excitation temperature in the discharge (about $4000\text{--}5000^\circ\text{K}$) is much higher than in the King oven.

REDUCTION OF THE SPECTROGRAM

When there were hooks on both sides of the spectral line, their measurement and reduction were performed by the usual method.¹⁴ However there are places in the calcium spectrum at which the lines are so crowded together that the hooks of individual lines cannot be separated. In such cases the reduction of the spectrogram is performed in the following manner.

1. Close doublet

(a) Hooks between the absorption lines are absent; absorption lines are clearly visible on the spectrogram ($\lambda\lambda 4434.960\text{--}4435.688$). This case, considered in detail by Rozhdestvenskii,¹⁴ leads to measurement of the distance from the absorption line to the outside hooks (δ_1 and δ_2), and computations are performed according to the formulas:

$$\beta_1 = \frac{\left(1 + \frac{\delta_1}{\varepsilon}\right)^2 - \left(\frac{\delta_2}{\varepsilon}\right)^2}{\left(1 + \frac{\varepsilon}{\delta_1}\right)^2 - \frac{1}{\left(1 + \frac{\varepsilon}{\delta_2}\right)^2}} \varepsilon^2, \quad \beta_2 = \frac{\left(1 + \frac{\delta_2}{\varepsilon}\right)^2 - \left(\frac{\delta_1}{\varepsilon}\right)^2}{\left(1 + \frac{\varepsilon}{\delta_2}\right)^2 - \frac{1}{\left(1 + \frac{\varepsilon}{\delta_1}\right)^2}} \varepsilon^2, \quad (1)$$

where ε is the distance between the lines, and β_1 and β_2 are quantities directly connected with the numbers Nf in the following way:

$$Nf = \frac{4\pi mc^2 k}{e^2 \lambda^3 d} \beta. \quad (2)$$

Here e and m are the charge and mass of the electron, c is the velocity of light, λ is the wavelength, d is the thickness of the absorbing vapor column, and k is a constant for the hook method.

(b) Hooks between the absorption lines are absent, the absorption lines are not resolvable ($\lambda\lambda 3630.748\text{--}3630.974$; $3350.209\text{--}3350.361$. The triplet $3361.918\text{--}3362.131\text{--}3362.28$ is a similar case, inasmuch as the last line is extremely weak and makes no significant contribution to the dispersion). In this case δ_1 and δ_2 cannot be measured, and we measure the quantity

$$\Delta = \delta_1 + \delta_2 + \varepsilon, \quad (3)$$

i.e., the distance between the outside hooks.

Going over from the measured quantity Δ to the quantities β_1 and β_2 is possible only when we know the ratio of the gf values for the components of the doublet:

$$\frac{gf_2}{gf_1} = C = \frac{\beta_2}{\beta_1}. \quad (4)$$

It has been shown in several papers^{3,5,15} that there is strong L-S coupling in the calcium spectrum. This is

also confirmed by our measurements, the results of which are shown in the Table below. Thus the ratio of f numbers is equal to the theoretical value, which also determines the value of the constant C .

Calculation of the quantities β for this case was performed by means of the formula:

$$\left(\frac{\delta_2}{\delta_1}\right)^2 = \frac{\frac{1}{\left(1 + \frac{\varepsilon}{\delta_2}\right)^2} + C}{1 + \frac{C}{\left(1 + \frac{\varepsilon}{\delta_1}\right)^2}}.$$

This equation, following directly from the theory of the hook method, is solved for δ_1 and δ_2 by the method of successive approximations. For the first approximation to a sufficient degree of accuracy,

$$\left(\frac{\delta_2}{\delta_1}\right)^2 = C.$$

The quantities δ_1 and δ_2 , computed from (3) and (6) solved simultaneously, were substituted in the right-hand part of (5), and a new, more accurate value of the quantity $(\delta_2/\delta_1)^2$ was found.

This operation was repeated until the last approximation differed from its predecessor by less than 1%. After this, the quantities β_1 and β_2 were computed by formulas (1).

It should be remarked that the f number of one of the lines of a doublet, computed in this way, cannot be considered as independently measured. (The oscillator strengths of such lines are marked with an asterisk in the Table.)

2. Close triplet

Hooks are formed only at one of the lines, on the outside of the triplet ($\lambda\lambda 4454.781$; 4455.887 ; 4456.612).

In this case, we measured δ_1 , the distance from the hook at the strongest line 4454.781 to the absorption line itself.

Taking the ratio of the f numbers of the lines of the triplet as being equal to the theoretical value,

$$f_1 : f_2 : f_3 = 1 : C_2 : C_3,$$

we have from the theory of the hook method

$$\beta_1 = \left(\frac{1}{\frac{1}{\delta_1^2} + \frac{C_2}{(\varepsilon_{12} + \delta_1)^2} + \frac{C_3}{(\varepsilon_{13} + \delta_1)^2}} \right),$$

where ε_{12} and ε_{13} correspond to the distances between the first and second and first and third lines of the triplet.

The quantities f_2 and f_3 were computed with the aid of relationship (7), with the value of β_1 known from (8).

The errors attached to our measurements can be divided into three groups, according to the phases of the work described above.

1. Relative f numbers of the lines beginning at the

λ	Transition	$j-j'$	$f_{O \text{ and } P}$	f_{Sch}	f_A	$f_F \text{ and } K$	f_P	$f_B \text{ and } D$	f_V	$g_{O \text{ and } P}$	$g_{Theor.}$
226.728	$4^1S-4^1P^\circ$	0-1	1000	—	1000	1000	1000	1000	1000	—	—
298.555	$4^1S-5^1P^\circ$	0-1	25.1	—	—	24.3	—	15.0	24.5	—	—
275.471	$4^1S-6^1P^\circ$	0-1	40.4	—	—	39.9	—	37.6	—	—	—
200.728	$4^1S-7^1P^\circ$	0-1	—	—	—	20.4	—	10.8	—	—	—
272.781	$4^1S-4^3P^\circ$	0-1	0.0279	0.210	—	—	0.0303	—	—	—	—
221.65	$4^1S-4p^{11}P^\circ$	0-1	—	—	—	—	—	—	—	—	—
217.66	$4^1S-4p^{33}D^\circ$	0-1	—	—	—	0.51	—	—	—	—	—
241.40	$4^1S-4p^{33}P^\circ$	0-1	—	—	—	0.029	—	—	—	—	—
		0-1	—	—	—	0.029	—	—	—	—	—
254.781	$4^3P^\circ-4^3D$	2-3	177	194	295	—	—	168	181	98.8	100
234.960		1-2	181	162	—	—	—	—	—	60.6	53.6
225.441		0-1	212	217	—	—	—	—	—	23.7	23.8
255.887		2-2	31.6*	34.7	—	—	—	—	—	17.7	17.9
235.686		1-1	56.7	54.0	—	—	—	—	—	19.0	17.9
256.612		2-1	2.1*	2.3	—	—	—	—	—	1.2	1.2
244.410	$4P^\circ-5^3D$	2-3	54.7	57.8	38.8	—	—	—	—	92.0	100
230.748		1-2	58.0	49.4	—	—	—	41.2	51.7	58.6	53.6
224.111		0-1	78.7	65.7	—	—	—	—	—	28.5	23.8
244.765		2-2	9.94*	10.3	—	—	—	—	—	16.7	17.9
230.974		1-1	19.4*	16.5	—	—	—	—	—	19.5	17.9
244.940		2-1	0.65*	0.69	—	—	—	—	—	1.2	1.2
261.918	$4^3P^\circ-6^3D$	2-3	28.7	—	30.1	—	—	—	—	91.5	100
250.209		1-2	30.0	—	—	—	—	—	—	57.3	53.6
244.513		0-1	45.3	—	—	—	—	—	—	28.9	23.8
262.131		2-2	5.14*	—	—	—	—	—	—	16.4	17.9
250.361		1-1	10.0*	—	—	—	—	—	—	19.1	17.9
262.28		2-1	0.34*	—	—	—	—	—	—	1.2	1.2
262.172	$4^3P^\circ-5^3S$	2-1	69.8	97.6	59.7	—	—	41.0	58.2	94.2	100
222.219		1-1	79.9	92.6	—	—	—	—	—	64.7	60
262.722		0-1	78.2	95.5	—	—	—	—	—	21.1	20
273.707	$4^3P^\circ-6^3S$	2-1	14.1	11.3	18.8	—	—	4.8	7.5	101.7	100
267.053		1-1	13.5	11.0	—	—	—	—	—	58.4	60
248.901		0-1	13.8*	10.2	—	—	—	—	—	19.9	20
262.527	$4^3P^\circ-4p^{23}P$	2-2	197	—	372	—	—	—	—	97.6	100
298.986		1-1	72.8	—	—	—	—	—	—	21.6	20
218.652		2-1	64.5	—	—	—	—	—	—	31.9	33.3
277.744		1-0	93.7	—	—	—	—	—	—	27.8	26.7
283.010		1-2	116	—	—	—	—	—	—	34.4	33.3
289.364		0-1	269	—	—	—	—	—	—	26.6	26.7

Note: Asterisks mark f numbers of one of the lines of a doublet which cannot be treated as independently measured.

normal level are defined with error not exceeding 3-4% for the strongest lines the error $<1\%$).

2. The errors in the relative f numbers of lines originating at the $4^3P_{0,1,2}$ level are less than 5%.

3. Reducing all lines to one scale involves calculation of the relative populations of the 4^1S_0 and $4^3P_{0,1,2}$ by levels by Boltzmann's formula, which leads to errors of 10-15% for the relative f numbers.

RESULTS AND DISCUSSION

The results of our measurements are shown in the Table. The first three columns give the wavelengths and series assignments of the spectral lines, taken from the tables of Moore.¹⁶⁻¹⁸ The next column of the Table gives the f numbers (f_0 and p) obtained in the present paper, the f number of the line 4226.728 being taken by us as 000. The absolute value of the f number of this line ($f_{4226.7} = 1.3$) was measured in ref. 19 so that the data of the Table can easily be converted to absolute f numbers. The remaining columns of the Table give the data of other authors, converted to a common scale: Schuttevaer³ (f_{sch}), Allen⁴ (f_A), Filippov and Kremnevskii² (f_F and k), and Prokofev¹ (f_P).

The Table also gives the results of the quantum-mechanical computations performed by us in a Coulomb approximation (f_B and D)²⁰ and by the semiempirical method (V) by Vainshtein.²¹

The last two columns of the Table give the intramultiplet ratios of the gf numbers obtained in the present paper (gf_0 and P) and taken from tables²² computed on the assumption of L-S coupling (gf_{theor}).

Whenever the data of other authors referred to the multiplet as a whole, these data were recomputed by us for the separate lines, using the theoretical intensity ratios given in the last column of the Table.

From the data given in the Table it follows that:

1. The results of all the measurements made by the hook method agree nicely among themselves. Thus it can be considered firmly established that the f numbers of the lines of the principal singlet series of calcium are non-monotonic functions of the principal quantum number (n).

2. The results of our measurements for lines of the diffuse and sharp series of calcium agree satisfactorily with the measurements of Schuttevaer. The average disagreement is about 15%, however it reaches 30-40% for several lines. The f number measured by Schuttevaer for the line $4^1S_0-4^3P_1$ (6573 Å) exceeds our value by a factor of about 8. The reason for this discrepancy is not clear. Reabsorption must have distorted Schuttevaer's results in the other direction. The errors of polychromatic photometry could hardly have been so large, besides which no systematic divergence of our data with Schuttevaer's as a function of wavelength is observed. One can only assume that errors were committed by Schuttevaer in measuring the temperature, or that there was a very unfavorable distribution of atomic concentrations and temperatures across the arc.

3. The results of Allen (with the exception of f_{4302}) coincide with our data to within his error of measurement ($\pm 60\%$).

4. The relative f numbers computed by the semi-empirical method agree well (except for f_{373}) with the measured values. However, the data obtained by the Bates-Daamgard method do not give such good agreement.

5. It is interesting to note the good agreement between the theoretical and observed values of g_f in the multiplets. This indicates that L-S coupling exists among the vectors in the calcium atom.

Note added in proof: The results of ref. 8, published in *Astrophys. J.* **130**, 688 (1959), are in very good agreement with our data. The average divergence is 10%. The results of the two papers differ by 30% for only two lines out of the 29.

REFERENCES

1. V. K. Prokof'ev, Zhur. Eksptl. i Teoret. Fiz. 1, 111 (1931).
2. A. N. Filippov and N. V. Kremnevskii, Fiz. Zhur. SSSR, 1, 299 (1932).
3. J. Schuttevaer, M. deBont, and M. van den Broek, Physica 10, 544 (1943).
4. C. W. Allen, Monthly Notices Roy. Astron. Soc. 117, 622 (1957).
5. E. Katz and L. Ornstein, Physica 4, 757 (1937).
6. A. G. Shenston and H. Russel, Phys. Rev. 39, 417 (1932).
7. L. Bovey and J. B. Birks, Brit. J. Appl. Phys. 11, 525 (1960).
8. R. King, B. Parnes, M. Davis, and K. Olsen, Proc. Conf. Stellar Atmospheres, p. 46, 1954.
9. D. S. Rozhdestvenskii and N. P. Penkin, J. Phys. USSR 5, 319 (1941).
10. Yu. I. Ostrovskii, G. F. Parchevskii, and N. P. Penkin, Opt. i Spektr. 1, 821 (1957).
11. Yu. I. Ostrovskii and N. P. Penkin, Opt. i Spektr. 3, 193 (1958).
12. N. P. Penkin, Zhur. Eksptl. i Teoret. Fiz. 17, 1114 (1947).
13. S. E. Frish, N. P. Penkin, and A. M. Shukhtin, Zhur. Eksp. Teoret. Fiz. 18, 734 (1948).
14. D. S. Rozhdestvenskii, Papers on Anomalous Dispersion in Metal Vapors. Leningrad, 1951.
15. H. Burger and H. Dorgelo, Z. Physik 22, 170 (1924); Ibid. 23, 258 (1924).
16. C. Moore, A Multiplet Table of Astrophysical Interest (revised ed.). I. Table of Multiplets, Contrib. Princeton Univ. Observatory No. 20, 1-110 (1945).
17. C. Moore, An Ultraviolet Multiplet Table, U.S. Natl. Bur. Standards Circ. No. 488, 1950.
18. C. Moore, Atomic Energy Levels as Derived from the Analysis of Optical Spectra. U.S. Natl. Bur. Standards Circ. No. 467, Atomic Energy Levels I, 1949.
19. Yu. I. Ostrovskii, N. P. Penkin, and L. N. Shabanova, Doklady Akad. Nauk SSSR 120, 66 (1958), Soviet Phys. Doklady 3, 538 (1959).
20. D. Bates and A. Daamgard, Phil. Trans., 242, 101, 1949.
21. L. A. Vainshtein, Opt. i Spektr. 3, 313 (1957).
22. E. Condon and G. Shortley, "Theory of Atomic Spectra." Cambridge Univ. Press, 1935.

INTERFEROMETRIC METHOD FOR THE DETERMINATION OF THE GAS DENSITY AND ELECTRON CONCENTRATION IN PLASMA

A. M. Shukhtin (pp. 436-442)

Received 23 May 1960

The possibility is examined of determining the gas density and electron concentration in a plasma by measuring the refractive index using the method of superposition of perturbed and undistorted interference patterns. Methods for the determination of small as well as large displacements of the pattern are described. Factors which determine the accuracy of the measurements are considered.

INTRODUCTION

It is well known that a change in the gas density, ionization, and excitation are accompanied by a change in the refractive index. These properties are widely applied for the determination of the gas density in flowing streams.¹ In refs. 2 and 3 these principles were applied to the determination of the gas density and electron concentration in open arcs and sparks. The magnitude of the change in the refractive index can be determined interferometrically from the shift of the interference pattern. In the usual arrangements of the interferometric method portions of the pattern corresponding to the undistorted and to the perturbed state of the gas are obtained on one photograph. The shift of the fringes is subsequently determined from such a photograph. However, if the process under investigation takes place in a closed container and the gas within the whole volume is perturbed, it is not possible to obtain simultaneously a photograph of the undistorted and the perturbed patterns. The above-mentioned method of observation based on the shift of the interference pattern is then not suitable and other procedures are necessary.

The methods which can be applied in such a case will differ somewhat for observation of large displacements

of the pattern, for example, of several fringes,⁴ and for shifts corresponding to a fraction of a fringe.

THE DETERMINATION OF ELECTRON CONCENTRATIONS AND CHANGES IN GAS DENSITY WHICH CAUSE A DISPLACEMENT OF THE PATTERN THROUGH SEVERAL FRINGES

Let us consider a two-beam interferometer, for instance, the Rozhdestvenskii interferometer.⁵ The object under investigation is placed in the path of one of the interfering parallel light beams and a compensator consisting of a tube with plane-parallel windows is placed in the path of the other beam. The interferometer is crossed with a spectrograph; the system is illuminated by a light source emitting a continuous spectrum. An interference pattern is observed in the focal plane of the spectrograph we shall call this the undistorted pattern. The perturbation of the gas is accompanied by a change in the interference pattern, namely by a shift of the interference fringes.

Let us assume that only a change in the density of magnitude $\Delta\rho$ occurs when the gas is perturbed.

The following equation will be assumed for the dispersion of the gas

$$n - 1 = A\rho. \quad (1)$$

The change in the optical path, expressed in wavelength can be written:

$$\mu = \frac{LA\Delta\rho}{\lambda}, \quad (2)$$

where L is the length of the column of gas under investigation. If $\Delta\rho$ is sufficiently large, for some wavelengths λ the change in the optical path will be equal to a whole number of wavelengths and for others it will be equal to an odd number of half-wavelengths. The undistorted and the perturbed interference patterns are now superimposed on one and the same part of a photographic film. For light of a wavelength corresponding to a shift of a whole number of fringes the maxima of different orders of the two patterns will coincide and we obtain a sharp portion of the pattern on the film. The maxima of one pattern coincide with the minima of the other at wavelengths which correspond to a change in optical path of an odd number of half-wavelengths; the pattern on the film becomes indistinct (diffuse) or a section with twice the number of fringes of equal intensity appears (Fig. 1).



Fig. 1. Spectrograms obtained when two interference patterns are superimposed. (The spectrograms were obtained by Yu. G. Kozlov and V. S. Egorov). a—Superimposed undisturbed patterns; b—the displacement is equal to half a fringe for wavelengths corresponding to the central part of the fringe; c—the displacement consists of several fringes; d—the patterns are displaced by more than one hundred fringes.

By taking photographs in this way over a large spectral region we obtain on the film alternating sharp and diffuse regions of the interference pattern. One can write the following set of equations for two diffuse regions in the pattern:

$$\left. \begin{aligned} LA\Delta\rho &= \frac{2k_1 + 1}{2} \lambda_1, \\ LA\Delta\rho &= \frac{2k_2 + 1}{2} \lambda_2, \\ k_2 &= k_1 + i. \end{aligned} \right\} \quad (3)$$

Here λ_1 and λ_2 are determined with the aid of a comparison spectrum; i is the number of sharp regions of the pattern between the two diffuse regions considered, and it is obtained from the spectrogram. The unknown quantities $\Delta\rho$, k_1 , and k_2 can be readily determined from Eqs. (3). If the change in refractive index is due to ionization one can determine the change in the electron concentration by applying the dispersion equation for an electron gas in a precisely analogous manner. In practice, the dispersion equation for an electron gas can be written as follows:

$$n - 1 = -\frac{N_e e^2}{2\pi m c^2} \lambda^2. \quad (4)$$

If we superimpose a pattern obtained in the absence

of electrons onto a pattern obtained in the presence of an electron concentration N_e , we will obtain spectrograms with a system of indistinct and sharp sections of interference fringes.

One can then write the following set of equations for two diffuse regions:

$$\left. \begin{aligned} \frac{LN_e e^2}{2\pi m c^2} \lambda_1 &= \frac{2k_1 + 1}{2}, \\ \frac{LN_e e^2}{2\pi m c^2} \lambda_2 &= \frac{2k_2 + 1}{2}, \\ k_2 &= k_1 + i. \end{aligned} \right\} \quad (5)$$

By measuring the wavelengths λ_1 and λ_2 and on counting the number i of sharp sections between the first and second diffuse region one can obtain the unknown quantities N_e , k_1 , and k_2 from Eqs. (5). It can be easily seen by comparing the sets of equations (3) and (5) that the diffuse regions which depend on a change in the density of the gas and on the appearance of an electron gas will be differently disposed on the spectrogram. When ρ is changing, the order of a diffuse region increases and the separation between diffuse regions decreases with a decrease in wavelength. This dependence on wavelength of the order and the separation of diffuse regions is exactly the opposite of that for diffuse regions which are caused by the appearance of an electron gas. Considerable electron concentrations are necessary to shift the interference pattern through several fringes. Such concentrations should arise, for instance, at the moment of compression of a plasma in strong pulsed discharges. According to ref. 6 electron concentrations of $N_e \approx 10^{17} \text{ cm}^{-3}$ were obtained at the moment of compression in some experiments with straight tubes of length $L \approx 100 \text{ cm}$. Under these conditions the shift of the pattern should amount to approximately 25 fringes at $\lambda = 6000 \text{ \AA}$.

This action on the gas can be accompanied by a simultaneous change in its density and ionization. If we superimpose the perturbed pattern onto the undistorted pattern we will again obtain spectrograms with successive sections of sharp and indistinct interference patterns. One can now write the following set of equations for the diffuse regions:

$$\left. \begin{aligned} LA\Delta\rho + \frac{LN_e e^2}{2\pi m c^2} \lambda_1^2 &= \frac{2k_1 + 1}{2} \lambda_1, \\ LA\Delta\rho + \frac{LN_e e^2}{2\pi m c^2} \lambda_2^2 &= \frac{2k_2 + 1}{2} \lambda_2, \\ LA\Delta\rho + \frac{LA_e e^2}{2\pi m c^2} \lambda_3^2 &= \frac{2k_3 + 1}{2} \lambda_3, \\ k_2 &= k_1 + i, \quad k_3 = k_1 + i_2. \end{aligned} \right\} \quad (6)$$

Having determined the location of three diffuse regions on the spectrogram and the numbers of sharp sections i_1 and i_2 one can calculate the electron concentration N_e , as well as the change in gas density $\Delta\rho$, by employing Eqs. (6). The above method is clearly suitable for the investigation of static processes as well as processes which consist of single pulses. In the latter case the light source yielding a continuous spectrum must be an intense short-duration flash which is synchronized with the process under investigation. The application of a narrow light beam and of short duration exposures synchronized with the pulses under investigation should permit the change in the electron concentration and gas density to be followed both in time and across the cross-section of the apparatus. For instance, according to ref. 6, during strong pulsed discharges in cylindrical tubes

the maximum concentration of the electrons at the moment of compression of the plasma occurs not on the axis, but at some distance from it. This phenomenon could be observed by using an interferometer of suitable base and passing one light beam along the axis and the second at the distance corresponding to the location of the expected maximum. The spectrogram in this case would permit the direct determination of the difference in electron concentrations on the axis and at the given distance from it.

THE DETERMINATION OF THE DIRECTION OF THE DISPLACEMENT OF THE INTERFERENCE PATTERN

Having determined the location of the diffuse regions in the spectrogram one can find the magnitude of the shift of the pattern, but it is impossible to say anything about the direction in which it takes place. By using the compensator in the following manner it is easy to determine the direction of the shift. We photograph the interference pattern with unperturbed gas in the compensator and in the tube under investigation. We then change the density of the gas in the compensator to some definite value and photograph the pattern at the instant of perturbation of the gas in the investigated volume, superimposing this second pattern onto the first. The sign of the change in gas density in the compensator is set by introducing gas into it, or, conversely, by pumping it out. If the signs of the changes in the gas density in the compensator and in the volume under investigation agree, the magnitude of the shift will be equal to the difference of the shift obtained separately by the changes in the density of the gas in the compensator and in the volume under test. If the signs are different the shift will be equal to the sum of the shifts. The equation which determines the locations of the diffuse regions caused by a change in the density of the gas in the compensator alone is given by:

$$\frac{L_0 A_0 \Delta \rho_0}{\lambda_{0k}} = \frac{2k+1}{2} \quad (7)$$

The equation which determines the location of the diffuse regions due to the joint effect of the changes of the gas density in the compensator and in the volume under study will be as follows:

$$\frac{L_0 A_0 \Delta \rho \mp L A \Delta \rho_x}{\lambda_k} = \frac{2k+1}{2} \quad (8)$$

Equations (7) and (8) will yield different values of λ for a given value of k . The equation for the displacement of the k -th diffuse region will be as follows:

$$\lambda_{0k} - \lambda_k = \pm \frac{2LA}{2k+1} \Delta \rho_x \quad (9)$$

The difference $(\lambda_{0k} - \lambda_k)$ can be positive as well as negative, that is, the k -th diffuse region can shift in the direction of short wavelengths or long wavelengths depending on the relative signs of $\Delta \rho_0$ and $\Delta \rho_x$.

The wavelength λ_{0k} can be calculated or measured from the spectrogram according to Eq. (7). The value of λ_k is determined from the spectrogram using Eq. (8). The magnitude and sign of the quantity $(\lambda_{0k} - \lambda_k)$ permit both the relative magnitude and the sign of the change in gas density $\Delta \rho_x$ to be determined.

THE DETERMINATION OF ELECTRON CONCENTRATIONS AND CHANGES IN GAS DENSITY WHICH CAUSE A SHIFT OF THE PATTERN OF A FRACTION OF A FRINGE

If the change in the density causes a shift of the pattern in the plane of the spectrum of less than half a fringe, the latter being readily observed, then the application of the method described above is difficult. The course to be followed in this case is indicated by Eq. (9). In fact, let us assume that we deal with a change in density $\Delta \rho_x$ which causes a shift of the pattern through a small fraction of a fringe k' in the part of the spectrum λ' under observation. Expressing $\Delta \rho_x$ in terms of k' , by employing Eq. (2) and substituting for it in Eq. (9), we get:

$$\lambda_{0k} - \lambda_k = \lambda' \frac{2k'}{2k+1} \quad (10)$$

Let us assume, for example, that $\lambda' = 5000 \text{ \AA}$ and $k' = 0.1$. Then the magnitude of the shift of the diffuse regions of the zero, first, second, and third order will be equal to 1000, 300, 200, and 140 $\text{\AA}$ respectively. The method of measurements can be approximately as follows. The volume under investigation is placed in the path of one of the beams and in the other beam is placed the compensator with a device which permits the pressure of the gas within it to be changed by a definite amount. Having established some initial gas density in the compensator, we photograph the interference pattern without producing a perturbation in the volume under investigation. We then change the density of the gas in the compensator and, producing the perturbation of the gas to be studied, we again photograph the interference pattern onto the same part of the film. We obtain on the photographic film a system of diffuse regions corresponding to the sum of the changes of density in the compensator and in the volume under investigation ($\Delta \rho_0 \pm \Delta \rho_k$). The quantity $\Delta \rho_0$ can be determined by measuring the change in the pressure of the gas in the compensator. However, one can also proceed differently. Let us assume that with the aid of the existing apparatus we can change the gas density in the compensator every time through one and the same accurately known quantity $\Delta \rho_0$. Using the above method, but not perturbing the gas in the volume under consideration, we can obtain calibration spectrograms with a system of diffuse regions corresponding to a change in gas density of magnitude $\Delta \rho_0$. Applying this calibration spectrogram and the spectrogram corresponding to the change in gas density of magnitude ($\Delta \rho_0 \pm \Delta \rho_x$), we arrive at the magnitude of the shift $(\lambda_{0k} - \lambda_k)$ for the diffuse regions of the corresponding order, and hence, with the aid of Eq. (9), at the magnitude of $\Delta \rho_x$.

The method examined above is suitable for the determination of small changes of density with small as well as large initial gas densities in the volume under investigation, and also for the determination of large changes in gas density.

The change in the optical path called forth by the appearance of an electron gas expressed in wavelengths, may be written

$$\frac{LN_e e^2}{2\pi m c^2} \lambda = k \quad (11)$$

The shift of the interference pattern expressed as a fraction of a fringe is given by this number k . If in the wavelength region which can be observed visually $k >$

2, one can employ the method of superposition of the undistorted and perturbed patterns in its usual form. If the electron concentration is small, a shift of 1/2 fringe will occur in the region of very long wavelengths and usual observations will be impossible in this case. But even it is possible to shift the system of diffuse regions towards shorter wavelengths which will be suitable for usual observation.

Let us assume that we perform the following operation. We photograph the pattern with the gas under investigation in an unperturbed state and with a certain gas density in the compensator. After that we superimpose onto it a second pattern after having reduced the pressure in the compensator by an amount $\Delta\rho_0$. On the photographic film we obtain a spectrogram with a system of diffuse regions conforming to expression (7).

If the second exposure is taken at the moment when, in addition to a reduction in gas density in the compensator, a perturbation of the gas in the volume under investigation takes place and free electrons of concentration N_e appear, a second system of diffuse regions will result which is governed by the expression

$$\frac{L_0 A_0 \Delta\rho_0}{\lambda_k} - \frac{LN_e e^2}{2\pi m c^2} \lambda_k = \frac{2k+1}{2}. \quad (12)$$

For a given value of N_e the diffuse regions evidently shift in the direction of short wavelengths. The magnitude of the shift of the k -th order diffuse regions will be equal to

$$\lambda_{0k} - \lambda_k = \frac{2}{2k+1} \cdot \frac{N_e e^2}{2\pi m c^2} \lambda_k^2. \quad (13)$$

Comparing Eqs. (13) and (9) we see that when the gas density is changed, the magnitude of the shift does not depend on the wavelength, whereas an electron gas results in a shift whose magnitude is proportional to λ^2 . For this reason, when determining the electron concentration by the above method, it is more convenient to observe the shift in the long wavelength end of the spectrum. Let us assume that the electron concentration and the length of the column under investigation are such that we obtain a shift of the pattern of one tenth of a fringe, i.e., $k'' = 0.1$ in the region $\lambda'' = 6000$ Å. We shall now determine the magnitude of the displacement. Let us assume, for instance, that a diffuse region with $k = 2$ occurred in the spectral region $\lambda_{02} = 6000$ Å. Using the expression (11) we shall rewrite Eq. (13) in the following way:

$$\lambda_{02} - \lambda_2 = \frac{2k''}{(2k+1)} \lambda''^2. \quad (14)$$

If we solve this equation we obtain $\lambda_2 = 5775$ Å and $(\lambda_2 - \lambda_{02}) = 225$ Å. Thus a displacement of 0.1 of a fringe in the region $\lambda = 6000$ Å caused by an electron gas produces a displacement of the diffuse region of the second order of 225 Å. For a cylinder of length $L = 100$ cm the electron concentration corresponding to these conditions will be $N_e = 4.3 \times 10^{14} \text{ cm}^{-3}$. The second root of Eq. (14) gives values of wavelengths of diffuse regions which would be formed in the far infrared or radio frequency regions of the spectrum. Let us assume that ionization of the gas and a change in its density occur simultaneously in the volume under investigation and that we desire to determine both quantities. We shall investigate changes which result in a shift of the interference pattern of a fraction of a fringe. In this case also the procedures examined above permit the desired quantities to be deter-

mined. Let us assume as before that the volume under investigation is placed in the path of one of the beams and that the compensator is placed in the path of the other. We photograph the interference pattern with gas in the unperturbed state and with a certain amount of gas in the compensator. We then reduce the density of the gas in the compensator by an amount $\Delta\rho_0$ and again take a photograph of the interference pattern onto the same part of the film. We obtain a calibration spectrogram with a system of diffuse regions subject to the expression (7). The next spectrogram we shall obtain in the following way. We shall again take a photograph of the interference pattern with the gas under investigation in the unperturbed state and an initial value of the gas density in the compensator. We then reduce the gas density in the compensator by the previous amount $\Delta\rho_0$, perturb the gas under investigation, and photograph the interference pattern onto the same part of the photographic film. We obtain a spectrogram with a system of diffuse regions satisfying the following relationship:

$$\frac{2k+1}{2} \frac{\lambda_{0k}}{\lambda_k} \pm \frac{LA\Delta\rho_x}{\lambda_k} - \frac{LN_e e^2}{2\pi m c^2} \lambda_k = \frac{2k+1}{2}. \quad (15)$$

We obtain the value of k from the calibration spectrogram and two unknown quantities, N_e and $\Delta\rho_x$, remain in the equation. Two equations, corresponding to two diffuse regions for which $k = k_1$ and $k = k_2$, must be written for their determination:

$$\left. \begin{aligned} \frac{2k_1+1}{2} (\lambda_{0k_1} - \lambda_{k_1}) &= LA\Delta\rho_x + \frac{LN_e e^2}{2\pi m c^2} \lambda_{k_1}^2, \\ \frac{2k_2+1}{2} (\lambda_{0k_2} - \lambda_{k_2}) &= LA\Delta\rho_x + \frac{LN_e e^2}{2\pi m c^2} \lambda_{k_2}^2. \end{aligned} \right\} \quad (16)$$

The unknown quantities $\Delta\rho_x$ and N_e can be determined from this system. We obtain the following relationship for the determination of the electron concentration:

$$(2k_1+1)(\lambda_{0k_1} - \lambda_{k_1}) - (2k_2+1)(\lambda_{0k_2} - \lambda_{k_2}) = \frac{LN_e e^2}{\pi m c^2} (\lambda_{k_1}^2 - \lambda_{k_2}^2). \quad (17)$$

Thus for the determination of N_e it is necessary to measure the wavelengths of two corresponding diffuse regions on two spectrograms and to substitute them in Eq. (17).

ON THE ACCURACY OF MEASUREMENT OF N_e AND $\Delta\rho$

As always, the accuracy of measurement of N_e and $\Delta\rho$ will be determined by the accuracy of the working formulas, the errors in measurement of the quantities which occur in them, and the influence of uncontrolled external disturbances. The location of the diffuse regions on the spectrogram are determined by direct measurements. Experiment shows that it is not difficult to determine the location of the diffuse regions of low orders from a good spectrogram with an accuracy such that the error in the determination of the shift of the pattern is less than 1/100 of a fringe. It is evident that in the majority of cases this will not set the limit on the accuracy of measurement.

The interferometric apparatus is sensitive to external mechanical influences. But the method requires the superposition of two interference patterns obtained at different times. The vibration of the apparatus leads to a displacement of one pattern with respect to the other.

The nature of the displacement of the pattern will be determined by the mechanical vibration of the system and will be the same as that during the change of the gas density. It is scarcely possible to separate these two forms of the shift within the framework of this method. Hence the accuracy of the measurement of the density of the gas will be determined chiefly by the mechanical arrangement of the interference system.

The nature of the shift of the pattern due to the appearance of an electron gas differs substantially from the shift caused by the vibrations of the system. It is easy to show that for this reason mechanical vibrations of the system should not introduce noticeable errors into the determination of electron concentration. When determining electron concentrations which cause small displacements of the pattern, substantial errors can result because of the approximate nature of the working formulas. Actually, when deriving formula (15) we assumed that the change in the refractive index during the perturbation of the gas depended only on the appearance of the electron gas and on the change in the number of unexcited atoms. For this reason formula (17) does not take into account the effect on the change of refractive index, for example, of the excited atoms. The effect of positive ions is also not taken into account. The appearance of unexcited ions can be looked upon as a change in the gas density and the latter does not have an effect on the accuracy of the determination of the electron concentration. The excited atoms and ions can change the refractive index in a different, more complicated manner. If we have a number of atoms N_i in an excited state i and if the numbers f_{ik} and wavelength λ_{ik} correspond to a transition from this state into a higher state, the dispersion equation will take the form

$$n - 1 = \frac{e^2 N_i f_{ik}}{2\pi m c^2} \cdot \frac{\lambda_{ik}^2 \lambda^2}{\lambda^2 - \lambda_{ik}^2}.$$

The displacement of the interference pattern at the wavelength λ caused by the appearance of atoms in the state i will be

$$k^* = \frac{e^2 N_i f_{ik} L}{2\pi m c^2} \cdot \frac{\lambda_{ik}^3 \lambda}{\lambda^2 - \lambda_{ik}^2}.$$

The sign of k will be different according to the sign of the difference $(\lambda - \lambda_{ik})$ and hence the shifts caused by the electron gas and the excited atoms will either add ($\lambda < \lambda_{ik}$) or subtract ($\lambda > \lambda_{ik}$). The relative magnitude of these two shifts may be expressed in the following way:

$$\frac{k^*}{k''} = \frac{N_i f_{ik}}{N_e} \cdot \frac{\lambda_{ik}^2}{\lambda^2 - \lambda_{ik}^2}.$$

Let us assume that $\lambda_{ik} = 7500 \text{ \AA}$, and that measurements were performed at $\lambda = 6000 \text{ \AA}$; we then get

$$\frac{k^*}{k''} \approx \frac{2.5 N_i f_{ik}}{N_e}.$$

Let us assume that $k^* = k''$ and that $f_{ik} = 0.1$, and therefore $N_i \approx 4N_e$; this means that if the number of excited atoms is close to the number of electrons, the displacement of the pattern caused by a single transition will be close to the shift caused by the electron gas. Because the number of transitions can approach several tens, the total effect of the excited atoms on the displacement of the pattern may be considerable. It can be easily seen that in a number of cases this circumstance will be the main obstacle to the determination by interferometric methods of those electron concentrations which give rise

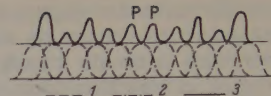


Fig. 2. Schematic diagram of the origin of the fringes observed in Fig. 1b. 1—Fringes of the first pattern; 2—fringes of the second pattern; 3—the observed fringes.

to small displacements of the pattern. If the transition lines in whose vicinity anomalous dispersion occurs are located in a region that can be observed visually, one can determine with the same apparatus the value of $N_{i f_{ik}}$ and hence estimate the effect of the excited atoms on the magnitude of the shift of the pattern.

The photograph in Fig. 1b represents a spectrogram obtained as a result of superposition of two displaced patterns. A displacement of half a fringe occurs in the central portion. The photograph has a strong background on which are located fine fringes with alternating intensities. The number of fringes is double the number on a single pattern. The origin of such a pattern can be easily understood with the aid of Fig. 2. The system of fringes corresponding to the two patterns are shown here schematically. The system of fringes corresponding to the fringes observed in the spectrogram is shown in the upper part of the drawing. The observed fringes do not belong to one of the original patterns but result from their joint action. In that region where the fringes of one pattern lie accurately in the middle, two small fringes FF of equal intensity are formed located between two fringes of the other pattern. To the right and left of these there will appear fringes with alternating intensities. Experiment shows that on a good spectrogram the fringes FF can be found and the desired wavelength can be determined with a precision of a few Angstroms. A very small error in the determination of the displacement corresponds to such an uncertainty in wavelength. For example, in the spectrogram corresponding to photograph b in Fig. 1 it is easy to indicate the position where the displacement is equal to $1/2$ fringe, with an uncertainty less than $\pm 1/500$ of a fringe.

In conclusion I would like to express my gratitude to S. E. Frish for valuable discussions and his interest in this work.

REFERENCES

1. "Fizicheskie izmereniya v gazovoi dinamike i pri goreniy" (Physical Measurements in Gaseous Dynamics and During Burning). Izd. Inostrannoi Lit., Moscow, 1957.
2. G. G. Dolgov and S. L. Mandel'shtam, Zhur. Eksptl. i Teoret. Fiz. 35, 691 (1958), Soviet Phys.-JETP 8, 480 (1959).
3. G. G. Dolgov and G. D. Petrov, Materialy X Vsesoyuz Soveshchaniya Spektr. (Proc. Tenth Natl. Conf. on Spectroscopy), Vol. 2, p. 68. L'vov University, 1958.
4. A. M. Shukhtin, Opt. i Spektr. 7, 839 (1960), Optics and Spectroscopy 7, 491 (1960).
5. D. S. Rozhdestvenskii, "Raboty po anomal'noi dispersii v parakh metallov" (On the Anomalous Dispersion in Metallic Vapors). Izd. Akad. Nauk SSSR, 1951.
6. L. A. Artsimovich, Uspekhi Fiz. Nauk 66, 545 (1958), Soviet Phys.-Uspekhi. 1, 191 (1958).

WAVE FUNCTIONS OF DIATOMIC MOLECULES WITH STRONG SPIN-ORBIT COUPLING

E. E. Nikitin (pp. 443-447)

Received 28 May 1960

In the existing theory of chemical bonding, and in present-day methods of calculating the wave functions of diatomic molecules, spin-orbit coupling is usually considered to be small in comparison with the coupling of the electron angular momentum with the molecular axis. The wave functions of the molecules thus correspond to Hund's type a or b coupling.¹ However, with increasing internuclear distance, the opposite relationship between these two interactions is always attained (Hund's case c). For molecules made up of light elements, this occurs only close to the dissociation limit (200-500 cm⁻¹), and as a result case c coupling does not enter into effects connected with the formation of a chemical bond. For heavy elements, however, the energy ϵ of the spin-orbit coupling may be of the order of magnitude of the binding energy E , and for large separations, which are of interest in many problems, may exceed it. In this case, generally speaking, many new effects related to spin-orbit coupling may appear.

The formation of a chemical bond appears as a tendency for the pairing (correlation) of the electron spins of different atoms. On the basis of the vector model of the atom, such a correlation is described by an antisymmetry in the spatial and spin coordinates of the wave function, which is the eigenfunction of the total spins of the individual electron pairs² (a function of the "valence structure").³ On the other hand, spin-orbit coupling destroys this correlation and, consequently, leads to a mixing of the structures associated with different values of the total spin. Moreover, spin-orbit coupling leads to a mixing of wave functions with different spatial symmetry such that it may be responsible for the nonadiabatic interaction of electron and nuclear motion within the molecule and for the strong dependence of the dipole moment of an electron transition on the internuclear distance.

In this connection it will be of interest to determine the wave functions which, in the first approximation, diagonalize the total Hamiltonian of two interacting atoms with strong spin-orbit coupling ($\epsilon \gg E$) so that corrections in the second approximation are of the order of E^2/ϵ .

Since the greatest interest experimentally is in the analogous molecules, let us consider the interaction of two identical atoms in the (p^5)²P_j state ($j = 1/2, 3/2$). An analogous problem was considered by Mulliken in ref. 4; however, the transformation matrix of the wave function from type a to type c coupling was not considered there in general form.

When $\epsilon \ll E$, the fine structure can be neglected, and the resulting state (ψ) is characterized by the quantum numbers and Λ and S (top line of Table 1). In the opposite case ($\epsilon \gg E$) the quantum number (state φ) is the projection of the total angular momentum Ω on the molecular axis (right-hand column of Table 1). The problem consists of calculating the matrix giving the connection between the wave functions $\varphi(j_1 j_2 \Omega)$ and $\psi(\Lambda, S)$ under the condition $\epsilon \gg E$. If we neglect the interaction of configurations in separated atoms and designate by

Table 1. Transformation Matrix of Wave Functions from Type a Coupling to Type c Coupling ($^2P_{j_1} + ^2P_{j_2}$)

$2P+2P$	$1\Sigma_g^+$	$3\Pi_u$	$1\Pi_u$	$3\Pi_g$	$1\Pi_g$	$3\Sigma_g^+$	$1\Delta_g$	$3\Sigma_g^-$	$1\Sigma_g^-$	$3\Delta_u$	$3\Sigma_u^+$	$1\Sigma_u^-$
$i_1 = i_2 = 3/2$	0_g	$2/3$		$\pm \sqrt{2}/3$				$1/\sqrt{2}$	$-1/3\sqrt{2}$			
	0_g		$+ \sqrt{2}/3$			$2/3$		$1/\sqrt{2}$	$1/\sqrt{2}$		$1/3\sqrt{2}$	$-1/3\sqrt{2}$
	0_u		$- \sqrt{2}/3$								$1/3\sqrt{2}$	$-1/3\sqrt{2}$
	0_u										$1/\sqrt{2}$	$1/\sqrt{2}$
	1_g			$1/\sqrt{3}$	$1/\sqrt{3}$			$1/\sqrt{3}$				
	1_u	$1/\sqrt{3}$	$1/\sqrt{3}$								$1/\sqrt{3}$	
	1_u	$\sqrt{2}/3$	$- \sqrt{2}/3$			$2/3$				$1/3$		
	2_g			$\sqrt{2}/3$			$1/\sqrt{3}$					
	2_u	$\sqrt{2}/3$								$1/\sqrt{3}$		
	3_u									1		
$i_1 = 3/2, i_2 = 1/2$	0_g	$2/3$		$-1/3\sqrt{2}$				$- \sqrt{2}/3$	$\sqrt{2}/3$			
	0_g		$+1/3\sqrt{2}$			$2/3$					$- \sqrt{2}/3$	$\sqrt{2}/3$
	0_u	$-1/3\sqrt{2}$										
	0_u	$\pm 1/\sqrt{2}$										
	1_g			$1/\sqrt{2}$	$-1/\sqrt{2}$							
	1_g			$1/\sqrt{6}$	$1/\sqrt{6}$			$- \sqrt{2}/3$				
	1_u	$1/\sqrt{6}$	$1/\sqrt{6}$								$- \sqrt{2}/3$	
	1_u	$1/3\sqrt{2}$	$-1/3\sqrt{2}$			$-2/3$				$2/3$		
	2_g			$-1/\sqrt{3}$			$\sqrt{2}/3$					
	2_u	$-1/\sqrt{3}$								$\sqrt{2}/3$		
$i_1 = 1/2, i_2 = 3/2$	0_g	$-1/3$		$\pm \sqrt{2}/3$				$- \sqrt{2}/3$	$\sqrt{2}/3$			
	0_u		$\pm \sqrt{2}/3$			$-1/3$					$- \sqrt{2}/3$	$\sqrt{2}/3$
	1_u	$- \sqrt{2}/3$	$\sqrt{2}/3$			$1/3$				$2/3$		
$E =$	$-1+4\gamma$		$1/2+5/2\gamma$		$1/2+9/2\gamma$		$1+4\gamma$		$2+\gamma$		$2+3\gamma$	

Note: When both spatial components of the Π state take part in the resolution of φ into ψ -functions, two signs are given: the upper for the positive spatial component, the lower for the negative one; the energy is expressed in units of I_σ ($\gamma = I_\pi/I$).

$\Phi(M_1 M_2 S_1 S_2)$ the appropriately antisymmetrized product of their wave functions with the orbital and spin projec-

tions M_1, s_1 and M_2, s_2 , then the following relationship holds for $\varphi(j_1 j_2 \Omega)$:

$$\varphi(j_1 j_2 \Omega) = \sum_{\substack{M_1 s_1 \\ M_2 s_2}} \left(j_1 \mu_1 \middle| 1 M_1 \frac{1}{2} s_1 \right) \left(j_2 \mu_2 \middle| 1 M_2 \frac{1}{2} s_2 \right) \Phi(M_1 M_2 s_1 s_2), \quad (1)$$

$$\Omega = \mu_1 + \mu_2,$$

where $(j_1 \mu_1 | 1 M_1 \frac{1}{2} s_1)$ are the Klebsch-Gordon coefficients. On the other hand, the functions $\psi(\Lambda, S)$ are expressed in terms of $\Phi(M_1 M_2 s_1 s_2)$ by an analogous equation

$$\psi(\Lambda, S) = \sum_{M_1 M_2} b(M_1 M_2) \sum_{s_1 s_2} \left(S_1 S_2 \middle| \frac{1}{2} s_1 \frac{1}{2} s_2 \right) \Phi(M_1 M_2 s_1 s_2), \quad (2)$$

in which the inner summation (over s_1, s_2) leads to an eigenfunction of the operator S^2 , and the outer one (over s_1, s_2) leads to a function of the given spatial symmetry. The exclusion of $\Phi(M_1 M_2 s_1 s_2)$ from (1) and (2) gives the desired transformation matrix. The results of the calculations are given in Tables 1 and 2.

Table 2. Transformation Matrix of Wave Functions from Type a Coupling to Type c Coupling (${}^2P_j + {}^2S_{1/2}$)

$2P + 3S$	${}^1\Sigma^+$	${}^3\Sigma^+$	1Π	3Π
$j_1 = \frac{3}{2}, j_2 = \frac{3}{2}$				
0	$\sqrt{\frac{2}{3}}$			$\pm \frac{1}{\sqrt{6}}$
0		$\sqrt{\frac{2}{3}}$		$\pm \frac{1}{\sqrt{6}}$
1		$\sqrt{\frac{2}{3}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$
1			$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
2				1
$j_1 = \frac{1}{2}, j_2 = \frac{3}{2}$				
0	$-\sqrt{\frac{1}{3}}$			$\pm \frac{1}{\sqrt{3}}$
0		$\sqrt{\frac{1}{3}}$		$-\frac{1}{3}$
1	$-\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{3}}$	$\sqrt{\frac{1}{3}}$	

On the basis of the data in Table 2, it is easy to explain the qualitative effect of spin-orbit coupling on the formation of a chemical bond. For weak spin-orbit coupling, the functions $\psi(\Lambda, S)$ diagonalize the Hamiltonian in the first approximation, in which case the diagonal matrix elements may be evaluated in conformity with the method of valence structure.³ A simple calculation shows that the ${}^1\Sigma^+$ state corresponds to the formation of a chemical bond, and that the remaining states lead to repulsion. With an increase in spin-orbit coupling, it is necessary to consider the interaction of the $0^{(1)}$ and $0^{(2)}$ states (the remaining states do not combine with these two). In this representation, the energy of the spin-orbit coupling enters into the diagonal terms, and the nondiagonal terms contain the matrix elements of the exchange interaction. By a straightforward calculation one is easily convinced that as a result of the interaction of the ${}^1\Sigma^+$ and ${}^3\Pi_0$ states the binding energy of the ground state is reduced; however, in this case a second bound state arises with a binding energy $D \approx \epsilon$ (a similar conclusion was drawn by Mulliken in ref. 4). The formation of an excited bound state as a result of spin-orbit coupling can clearly be discerned in the molecules F_2, Cl_2, Br_2 , and I_2 (ϵ is equal to 407, 881, 3685, and 7598 cm^{-1} , respec-

tively), whose absorption spectra (${}^1\Sigma_g^+ \rightarrow {}^3\Pi_{u,0}$) change from a continuum for F_2 to clearly expressed bands for I_2 .⁵

Recently, Vanderslice et al.,⁶⁻⁸ using a semiempirical method of valence schemes, calculated the asymptotic behavior of all the potential curves of the molecules N_2, NO , and O_2 which converge to the lowest dissociation limit of these molecules. The two exchange integrals I_σ and I_π were used as empirical parameters; the overlap integral S was not taken into consideration. It is easy to see, however, that this semiempirical method of calculation leads to errors of the order of S^4 , and not S^2 as follows from the Heitler-London formula. This is apparently the reason for the successful application of the method of valence schemes neglecting overlap. Unfortunately, this method is not applicable to the calculation of the spectrum of the I_2 molecule. Actually, if the overlap integrals are neglected, the ${}^3\Pi_{1u}$ and ${}^3\Pi_{2u}$ states, in contradiction to experimental data, are found to be not stable.* We note,

*Calculation of the overlap integrals within the framework of the semiempirical method would permit the introduction of two new parameters which would improve the agreement with experiment, since they decrease the binding energy of the ground state and increase the binding energy of the excited states. Nevertheless, the use of a four-parameter expression for the description of the I_2 spectrum does not seem expedient at present.

however, that without calculation of overlap the correct order of distribution of terms is obtained, and also, as is experimentally observable, the binding energy of the state 0_u ($j_1 = 1/2, j_2 = 3/2$) is larger than the binding energies of the states 1_u ($j_1 = j_2 = 3/2$) and 2_u ($j_1 = j_2 = 3/2$), which are components of the term ${}^3\Pi_u$. These and other qualitative conclusions can be obtained on the basis of first-approximation calculations of the energy with the functions $\varphi(j_1 j_2 \Omega)$ by using the values given in Table 1 for the exchange energies of states with quantum numbers Λ and S , which were calculated by the method suggested in ref. 6.

I wish to thank N. D. Sokolov for discussion of this work.

REFERENCES

1. G. Herzberg, "Spektry i Stroenie Dvukhatomnykh Molekul." Izd. Inostrannoi Lit., Moscow, Leningrad, 1949. Translation of "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules." 2nd ed., Van Nostrand, New York, 1950.
2. E. M. Corson, "Perturbation Methods in the Quantum Mechanics of n-Electron Systems." Hafner, New York, 1950.
3. H. Eyring, J. Walter, and G. Kimball, "Quantum Chemistry." Wiley, New York, 1944.
4. R. S. Mulliken, Phys. Rev. **57**, 500 (1940).
5. A. Gaydon, "Energija Dissotsiatsii i Spektry Dvukhatomnykh Molekul" (Dissociation Energies and Spectra of Diatomic Molecules). Izd. Inostrannoi Lit., Moscow, Leningrad, 1949. Wiley, New York, 1947; Chapman, London.
6. J. T. Vanderslice, E. A. Mason, and E. R. Lippincott, J. Chem. Phys. **30**, 129 (1959).
7. J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. **31**, 738 (1959).
8. J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. **32**, 515 (1960).

INFLUENCE OF THE ROTATIONAL STRUCTURE OF MOLECULAR BANDS ON LIGHT ABSORPTION BY LAYERS OF FINITE THICKNESS

V. N. Soshnikov (pp. 448-456)

Received 30 May 1960

We have carried out a numerical calculation for a model consisting of a random distribution of rotational lines of Lorentz-Doppler shape with a Boltzmann intensity distribution. We present a comparison with the model of equally intense lines and with the case of an exponential intensity distribution. We discuss the possibility and method of applying to a real spectrum the relationships derived here.

INTRODUCTION

In refs. 1 and 2, the models of a set of rotational lines with constant intensity and with an exponential intensity distribution are examined and compared, a dispersion line shape being assumed in the latter case. For lines with a dispersion contour, an exponential distribution, with the probability that the absorption coefficient at the maximum falls within the interval k_0^L to $k_0^L + dk_0^L$ being

$$dw(k_0^L) = \frac{1}{(k_0^L)_{av.}} e^{-\frac{k_0^L}{(k_0^L)_{av.}}} dk_0^L, \quad (1)$$

where $(k_0^L)_{av.}$ is the average absorption coefficient at the maximum, is chosen only because in this case it is possible to carry out an exact integration, of which the simple formula $(10)^{1-3}$ is the result. It is of interest to examine also the more general case of a Doppler-dispersion line shape with the more realistic Boltzmann intensity distribution.

RANDOM LINE DISTRIBUTION

Let us define $k_{av.}^{meas.}$ by the relation

$$e^{-k_{av.}^{meas.} l} = \overline{e^{-k(\nu)l}},$$

where $k(\nu)$ is the absorption coefficient as a function of the wave number ν , the average on the right-hand side being taken within a certain interval $\Delta\nu \equiv s$ over all possible arrangements of the rotational lines, which are distributed over the whole scale of wave numbers ν . It is evident that $k_{av.}^{meas.}$ is approximately the average absorption coefficient measured within a given spectral re-

gion by an apparatus with a sufficiently wide* spectral

*A sufficiently large number of lines must fall within the slit to make it possible to consider $\ln(I/I_0) \cong \ln(I/I_0)$, where the averaging is performed over the various line arrangements.

slit s of rectangular shape.

Since an inaccuracy* slipped into ref. 2 during ex-

*The situation in which there is a random distribution of m lines within the interval s , but lines beyond the limits of s are not taken into account, is hardly of practical interest. In Plass's article,² the expression under the integral sign in the starting formula (17), which is analogous to our (2) for $k_{av.}^{meas.}(\sigma)$, is considered to depend not on the differences $(\nu - \nu_1)$, but (erroneously) on ν_1 , on which account an additional integration $\int_{-s/2}^{s/2} d\nu$ was omitted. Consequently, in Plass's work the question arises, and is incorrectly treated, of the determination of the average absorption in the interval $\Delta\nu$ in the case of "a finite number of lines" in this interval. Subsequently, Plass goes over to the limiting case of "an infinite number of lines," $\Delta\nu \rightarrow \infty$. The formula (26) thus obtained is equivalent to our formula (3).

amination of the random model, we shall present a derivation of the appropriate formula for $k_{av.}^{meas.}$.

Let ρ be the average distance between rotational lines. With a random arrangement, the probability of finding an individual line i in the wave number interval ν_i to $\nu_i + d\nu_i$ is proportional to $d\nu_i$, and the desired average on measurement over the interval s with an arbitrary arrangement of n rotational lines in an interval $\sigma = \rho n > s$ is determined by the expression

$$k_{av.}^{meas.}(\sigma) = -\frac{1}{l} \ln \left\{ \frac{1}{s} \int_{-\frac{s}{2}}^{\frac{s}{2}} d\nu \left[\frac{1}{\sigma^n} \int_{-\frac{\sigma}{2}}^{\frac{\sigma}{2}} \dots \int_{-\frac{\sigma}{2}}^{\frac{\sigma}{2}} e^{-\sum_{i=1}^n k_i(\nu - \nu_i)} d\nu_1 \dots d\nu_n \right] \right\}. \quad (2)$$

Introducing the variables $\xi_i = \nu - \nu_i$, we get

$$k_{av.}^{meas.}(\sigma) = -\frac{1}{l} \ln \left\{ \frac{1}{s\sigma^n} \int_{-\frac{s}{2}}^{\frac{s}{2}} d\nu \int_{\nu - \frac{\sigma}{2}}^{\nu + \frac{\sigma}{2}} \dots \int_{\nu - \frac{\sigma}{2}}^{\nu + \frac{\sigma}{2}} e^{-\sum_{i=1}^n k_i(\xi_i)} d\xi_1 \dots d\xi_n \right\} = -\frac{1}{l} \ln \left\{ \frac{1}{s} \int_{-\frac{s}{2}}^{\frac{s}{2}} d\nu \prod_{i=1}^n \left[-\frac{1}{\sigma} \int_{\nu - \frac{\sigma}{2}}^{\nu + \frac{\sigma}{2}} (1 - e^{-k_i(\xi)}) d\xi + 1 \right] \right\}.$$

Going over to the limit $\sigma \rightarrow \infty$, we get

$$k_{av.}^{meas.} = \lim_{\sigma \rightarrow \infty} k_{av.}^{meas.}(\sigma) = -\frac{1}{l} \lim_{\sigma \rightarrow \infty} \sum_{i=1}^{\frac{\sigma}{p}} \ln \left[-\frac{1}{\sigma} \int_{-\infty}^{\infty} (1 - e^{-lk\xi}) d\xi + 1 \right] = \frac{1}{l_p} [W_i(l)]_{av.}, \quad (3)$$

where the quantity

$$W_i(l) = \int_{-\infty}^{\infty} (1 - e^{-lk\xi}) d\xi$$

is called the equivalent width for the i -th line.² We shall use the expression for $k(\xi)$ of an individual rotational line,⁴

$$k(\xi) = k_0 \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a^2 + (\omega - y)^2},$$

where

$$\omega = \frac{2\xi}{\Delta_D} \sqrt{\ln 2}, \quad a = \frac{\Delta_c}{\Delta_D} \sqrt{\ln 2},$$

Δ_c and Δ_D being respectively the collision and Doppler widths⁴ and k_0 the maximum absorption coefficient for Doppler line broadening only.

Setting

$$W_i(l) = \left[\frac{\Delta_D}{2\sqrt{\ln 2}} \zeta(a, x) \right]_i,$$

we obtain

$$k_{av.}^{meas.} = \left[\frac{\Delta_D}{2\sqrt{\ln 2} \rho l} \zeta(a, x) \right]_{av.}, \quad (4)$$

where $x \equiv k_0 l$. In Table 1 are presented the values of $\zeta(a, x)$, obtained on the basis of the asymptotic formulas⁴ with the help of numerical integration, and compared with the data of ref. 5. The error in the listed values of $\zeta(a, x)$ does not exceed 5%.

It follows from the data presented that, for small x or large a , $\zeta(a, x) \approx x\sqrt{\pi}$ ("linear region"), while for large x and $a \neq 0$, $\zeta(a, x) \approx 2\sqrt{ax}\sqrt{\pi}$ ("square root region").

We note in connection with this a general property of the relation (4): on carrying out an arbitrary breakdown of the n lines in the interval $\Delta\nu = \sigma = \rho n$ into sets a, b ,

c, ... of randomly distributed lines, we obtain in the limit as $\sigma \rightarrow \infty$,

$$k_{av.}^{meas.} = \frac{1}{l_p} [W_i(l)]_{cp.} = \frac{1}{l} \frac{\sum_{i=1}^n W_i(l)}{\sigma} = (k_{av.}^{meas.})_a + (k_{av.}^{meas.})_b + (k_{av.}^{meas.})_c + \dots \quad (5)$$

In particular, this relationship is applicable to the superposition of the random model and a continuous constant background.

AVERAGING OVER THE INTENSITIES

Let us consider an intensity distribution analogous to the distribution in the rotational lines of the electronic-vibrational bands of a diatomic molecule⁶ (see Figure),

$$k_0 \approx R j e^{-\alpha j^2}.$$

Here $\alpha \equiv B''/kT$, B'' is the rotational constant for the lower electronic state of the molecule, j numbers the lines, and $R \equiv k_{0\max} \sqrt{2\alpha e}$, where $k_{0\max}$ corresponds to the value $j = j_0 = \sqrt{1/2\alpha}$. The probability that a line has an intensity in the interval k_0 to $k_0 + dk_0$ is evidently proportional to $|dj/dk_0|$. Summing over both branches, we get

$$dw(k_0) = \left\{ \frac{C}{R} \frac{e^{j^2 \alpha}}{1 - 2\alpha j^2(k_0)} \right\}_{j < j_0} + \left\{ \frac{C}{R} \frac{e^{j^2 \alpha}}{2\alpha j^2(k_0) - 1} \right\}_{j > j_0} |dk_0|,$$

where the constant C is determined by normalization.

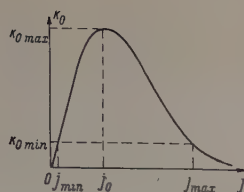
The indicated distribution is curious in that, as $k_0 \rightarrow 0$, $dw(k_0)/|dk_0| \rightarrow \infty$, which corresponds to an infinite crowding of the lines ($\rho \rightarrow 0$) (the intensity of the "lines" as $j \rightarrow \infty$ tends to zero together with the contribution made by them to the value of $k_{av.}^{meas.}$). With the choice of the intensity interval as $(k_{0\max}, k_{0\min})$, the normalizing factor $1/C$ equals the total number of lines $j_{\max} - j_{\min}$. Since

$$k_{av.}^{meas.} = \frac{\Delta_D}{2\sqrt{\ln 2} \rho l} \int_{k_{0\min}}^{k_{0\max}} \zeta(a, k_0 l) w(k_0) |dk_0|, \quad (6)$$

Table 1. Values of $\zeta(a, x)$

$a \backslash x$	1 ⁻¹	3 ⁻¹	1	3	10	3 ¹	1 ¹	3 ²	1 ²	3 ³	1 ³	3 ⁴	1 ⁴	3 ⁵	1 ⁵	3 ⁶	1 ⁶
0	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.3	4.0	4.5	5.0	5.5	5.8	6.3	6.6	6.9	7.3	7.6	7.9	8.2
1 ⁻⁵	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.3	4.0	4.5	5.0	5.5	5.9	6.3	6.7	7.3	8.1	1.05 ¹	1.50 ¹	2.7 ¹
3 ⁻⁵	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.3	4.0	4.5	5.0	5.5	5.9	6.4	6.9	7.9	9.9	1.50 ¹	2.5 ¹	4.6 ¹
1 ⁻⁴	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.3	4.0	4.5	5.0	5.5	6.0	6.6	7.6	1.00 ¹	1.50 ¹	2.7 ¹	4.6 ¹	8.4 ¹
3 ⁻⁴	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.3	4.0	4.5	5.0	5.6	6.2	7.3	9.6	1.50 ¹	2.5 ¹	4.6 ¹	8.0 ¹	1.45 ²
1 ⁻³	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.3	4.0	4.6	5.1	5.8	7.0	9.7	1.50 ¹	2.7 ¹	4.6 ¹	8.4 ¹	1.45 ²	2.7 ²
3 ⁻³	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.4	4.0	4.7	5.4	6.8	9.1	1.50 ¹	2.5 ¹	4.6 ¹	8.0 ¹	1.45 ²	2.5 ²	4.6 ²
1 ⁻²	1.70 ⁻¹	4.8 ⁻¹	1.30	2.4	3.4	4.1	5.1	6.4	9.3	1.40 ¹	2.7 ¹	4.6 ¹	8.4 ¹	1.45 ²	2.7 ²	4.6 ²	8.4 ²
3 ⁻²	1.70 ⁻¹	4.8 ⁻¹	1.30	2.5	3.6	4.6	6.1	8.8	1.40 ¹	2.5 ¹	4.6 ¹	8.4 ¹	1.45 ²	2.7 ²	4.6 ²	8.4 ²	1.45 ³
1 ⁻¹	1.70 ⁻¹	4.8 ⁻¹	1.30	2.6	4.1	5.8	1.0	1.40 ¹	2.7 ¹	4.6 ¹	8.4 ¹	1.45 ²	2.7 ²	4.6 ²	8.4 ²	1.45 ³	2.65 ³
3 ⁻¹	1.75 ⁻¹	5.0 ⁻¹	1.45	3.1	5.5	8.6	1.40 ¹	2.5 ¹	4.6 ¹	8.0 ¹	1.45 ²	2.5 ²	4.6 ²	8.0 ²	1.45 ³	2.5 ³	4.6 ³
1	1.80 ⁻¹	5.3 ⁻¹	1.55	3.8	8.0	1.35 ¹	2.7 ¹	4.6 ¹	8.4 ¹	1.45 ²	2.7 ²	4.6 ²	8.4 ²	1.45 ³	2.7 ³	4.6 ³	8.4 ³
3	1.80 ⁻¹	5.3 ⁻¹	1.80	4.6	1.20 ¹	2.4 ¹	4.6 ¹	8.0 ¹	1.45 ²	2.5 ²	4.6 ²	8.0 ²	1.45 ³	2.5 ³	4.6 ³	8.0 ³	1.45 ⁴
10	1.80 ⁻¹	5.3 ⁻¹	1.80	5.3	1.60 ¹	3.8 ¹	8.0 ¹	1.45 ²	2.7 ²	4.6 ²	8.4 ²	1.45 ³	2.7 ³	4.6 ³	8.4 ³	1.45 ⁴	2.7 ⁴
3 ¹	1.80 ⁻¹	5.3 ⁻¹	1.80	5.3	1.80 ¹	4.4 ¹	1.20 ²	2.4 ²	4.6 ²	8.0 ²	1.45 ³	2.5 ³	4.6 ³	8.0 ³	1.45 ⁴	2.5 ⁴	4.6 ⁴
1 ²	1.80 ⁻¹	5.3 ⁻¹	1.80	5.3	1.80 ¹	5.3 ¹	1.60 ²	3.8 ²	8.0 ²	1.45 ³	2.7 ³	4.6 ³	8.4 ³	1.45 ⁴	2.7 ⁴	4.6 ⁴	8.4 ⁴

Note: The region of applicability of the linear approximation is marked off at the lower left, the square root region at the right. The indices on the numbers denote powers of ten (for example, $1.80^{-1} = 1.80 \times 10^{-1}$).



Intensity distribution in a vibrational band as a function of the rotational quantum number j .

$$k_{av} = \frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} \Delta_D \frac{1}{\rho} \int_{k_0 \min}^{k_0 \max} k_0 \omega(k_0) |dk_0|, \quad (7)$$

where k_{av} is the average absorption coefficient in the given spectral region,⁴ then, substituting the expression for dk_0 in terms of j for the first and second branches respectively, we obtain

$$\begin{aligned} \frac{k_{av}^{meas.}}{k_{av}} &= \frac{1}{Rl \sqrt{\pi}} \frac{\int_{(k_0 \min)}^{(k_0 \max)} \zeta(a, k_0 l) (dj_I + dj_{II})}{\int_{(k_0 \min)}^{(k_0 \max)} \left\{ j_I e^{-\alpha j_I^2} dj_I + j_{II} e^{-\alpha j_{II}^2} dj_{II} \right\}} \\ &= \frac{1}{Rl \sqrt{\pi}} \frac{\int_{j_{\min}}^{j_{\max}} \zeta(a, l k_0) dj}{\int_{j_{\min}}^{j_{\max}} j e^{-\alpha j^2} dj} \end{aligned}$$

After substituting $\varphi = Rjl$ and going over to the limit $k_0 \min \rightarrow 0$, we have

$$\begin{aligned} \frac{k_{av}^{meas.}}{k_{av}} &= \frac{2a}{R^2 l^2 \sqrt{\pi}} \int_0^\infty \zeta(a, \varphi e^{-\beta \varphi^2}) d\varphi = \\ &= \frac{2\beta}{\sqrt{\pi}} \int_0^\infty \zeta(a, \varphi e^{-\beta \varphi^2}) d\varphi \equiv F\left(a, \sqrt{\frac{1}{\beta}}\right) \equiv F(a)(k_0 \max l), \end{aligned}$$

Table 2. Values of $F(a, \sqrt{1/\beta}) = k_{av}^{meas.}/k_{av}$.

$\sqrt{\frac{1}{\beta}}$	1	3.16	10	3.16 ²	1 ²	3.16 ³	1 ³	3.16 ⁴	1 ⁴	3.16 ⁵	1 ⁵	3.16 ⁶	1 ⁶	3.16 ⁷	1 ⁷	3.16 ⁸
β	1	1 ⁻¹	1 ⁻²	1 ⁻³	1 ⁻⁴	1 ⁻⁵	1 ⁻⁶	1 ⁻⁷	1 ⁻⁸	1 ⁻⁹	1 ⁻¹⁰	1 ⁻¹¹	1 ⁻¹²	1 ⁻¹³	1 ⁻¹⁴	1 ⁻¹⁵
0	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.6-2	1.35-2	5.0-3	1.80-3	6.3-4	2.2-4	7.6-5	2.6-5	8.9-6	3.0-6	1.00-6
1-5	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.6-2	1.35-2	5.0-3	1.80-3	6.3-4	2.2-4	7.6-5	2.6-5	1.05-5	4.3-6	2.1-6
3-5	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.6-2	1.35-2	5.0-3	1.80-3	6.3-4	2.2-4	8.1-5	3.1-5	1.30-5	6.2-6	3.2-6
1-4	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.6-2	1.35-2	5.0-3	1.85-3	6.5-4	2.4-4	9.2-5	4.0-5	2.00-5	1.00-6	5.6-6
3-4	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.6-2	1.35-2	5.1-3	1.90-3	6.8-4	2.7-4	1.20-4	6.1-5	3.2-5	1.70-5	9.5-6
1-3	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.6-2	1.35-2	5.2-3	2.00-3	8.3-4	3.7-4	1.85-4	1.00-4	5.5-5	3.1-5	1.75-5
3-3	8.8-1	7.3-1	4.6-1	2.2-1	9.2-2	3.7-2	1.45-2	5.7-3	2.4-3	1.10-3	5.7-4	3.1-4	1.70-4	9.5-5	5.4-5	3.0-5
1-2	8.8-1	7.3-1	4.6-1	2.2-1	9.6-2	4.0-2	1.60-2	7.1-3	3.4-3	1.80-3	9.8-4	5.5-4	3.1-4	1.75-4	9.8-5	5.5-5
3-2	8.8-1	7.3-1	4.7-1	2.4-1	1.05-1	4.6-2	2.05-2	1.01-2	5.4-3	3.0-3	1.70-3	9.5-4	5.4-4	3.0-4	1.70-4	9.5-5
1-1	8.8-1	7.6-1	5.0-1	2.7-1	1.30-1	6.2-2	3.1-2	1.75-2	9.8-3	5.5-3	3.1-3	1.75-3	9.8-4	5.5-4	3.1-4	1.75-4
3-1	9.1-1	8.0-1	5.9-1	3.2-1	1.80-1	9.7-2	5.3-2	3.0-2	1.70-2	9.5-3	5.4-3	3.0-3	1.70-3	9.5-4	5.4-4	3.0-4
1	9.6-1	8.8-1	7.0-1	4.8-1	2.8-1	1.70-1	9.5-2	5.4-2	3.0-2	1.75-2	9.8-3	5.5-3	3.1-3	1.75-3	9.8-4	5.5-4
3	9.8-1	9.6-1	8.7-1	6.8-1	4.9-1	2.9-1	1.65-1	9.4-2	5.3-2	3.0-2	1.70-2	9.5-3	5.4-3	3.0-3	1.70-3	9.5-4
10	1.00	9.8-1	9.6-1	8.8-1	7.0-1	4.8-1	2.8-1	1.70-1	9.6-2	5.4-2	3.1-2	1.75-2	9.8-3	5.5-3	3.1-3	1.75-3
31	1.00	1.00	1.00	9.7-1	8.5-1	6.8-1	4.6-1	2.8-1	1.65-1	9.4-2	5.3-2	3.0-2	1.70-2	9.5-3	5.4-3	3.0-3
12	1.00	1.00	1.00	1.00	9.8-1	8.8-1	7.0-1	4.8-1	2.9-1	1.70-1	9.6-2	5.5-2	3.1-2	1.75-2	9.8-3	5.5-3

Note: The square root region is marked off at the right. See note to Table 1.

where

$$\beta = \frac{a}{R^2 l^2} = \frac{1}{2ek_0^2 \max l^2}.$$

In the linear region (for large β).

$$F\left(a, \sqrt{\frac{1}{\beta}}\right) \approx 1:$$

in the square root region (for small β), integration gives

$$F\left(a, \sqrt{\frac{1}{\beta}}\right) = a^{\frac{1}{2}} \beta^{\frac{1}{4}} L,$$

where

$$L = \frac{2^{\frac{15}{4}}}{3\pi^{\frac{1}{4}}} \Gamma\left(\frac{7}{4}\right) \approx 3.10.$$

The values of $F(a, \sqrt{1/\beta})$ obtained by numerical integration are represented in Table 2 (the error does not exceed 5%).

APPLICATION TO A REAL SPECTRUM

The application to a real spectrum of both the model examined here and the others which have been studied is, after all, of a highly approximate character. We shall consider the practically important case of the radiation of an equilibrium molecular gas heated to a temperature of $\sim 4000^\circ\text{K}$ and higher. The random model may be applied, since a large number of irregularly disposed vibrational bands generally take part in radiation. The intensity of radiation by a gas layer of thickness l in the direction perpendicular to its surface is given by the expression⁷

$$I_v \Delta v = B_v (1 - e^{-k_{av}^{meas.} l}) \Delta v,$$

where I_v is the radiation intensity of a unit surface in a unit solid angle over a unit wave number interval; B_v is the radiation intensity of an absolutely black body:

$$B_v = \frac{2hc^2 \nu^3}{e^{h\nu/kT} - 1}.$$

Numerical estimates, taking (5) into account, show that, in the case of superposition of models with different intensities $k_{0\max}$, one may make use of the approximate formula

$$k_{av}^{(e)} \approx k_{av} F^{(a)} [(k_{0\max})_{av} l]. \quad (8)$$

For example, in the case of two models with a ten-fold difference,

$$\frac{k_{av}^{(1)}}{k_{av}^{(2)}} = \frac{k_{0\max}^{(1)}}{k_{0\max}^{(2)}} = 10,$$

the error in (8) amounts to not more than 20% on the high side. For the absorption intensity of the rotational line j_0 , which corresponds to the electronic transition from the lower vibrational level v'' to the upper one v' , we have^{4,7}

$$k_{0\max}^{(v'')} = \frac{2}{\Delta_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\pi e^2}{mc^2} n_0 f_e \frac{\nu}{\nu_{\max}} q_{v'}, q_{v''} w_{v''} w_{j_0} \left(1 - e^{-\frac{hc\nu}{kT}}\right).$$

Here $q_{v'}, v''$ is the square of the vibrational matrix element; $w_{v''}$ and w_{j_0} are respectively the vibrational and rotational Boltzmann factors, being

$$w_{v''} = e^{-\frac{v''}{kT}} \left(1 - e^{-\frac{v''}{kT}}\right), \quad w_{j_0} = 2aj_0 e^{-\frac{j_0^2}{2kT}} = \sqrt{\frac{2B''}{ekT}};$$

ω'' is the vibrational frequency; $\varepsilon_{v''}$ is the vibrational energy in the lower electronic state; n_0 is the concentration of absorbing molecules, and f_e is the electronic oscillator strength of the given electronic-vibrational band system;

$$f_e = \frac{8\pi^2 mc}{3h} R_e^2 \nu_{\max}^2,$$

where R_e^2 is the square of the electronic moment of the transition; ν is the wave number of the transition; $\nu_{\max}$ is the wave number corresponding to the maximum absorption intensity in the electronic system under consideration; and r is the square of the rotational matrix element, which, having in mind the averaging over the rotational branches, we replace by $1/\eta$ (here η is approximately the number of rotational branches of the band which take part in absorption, allowing for Λ -doubling, multiplet splitting, etc.).

To find the magnitude of $(k_{0\max})_{av}$, we make use of the relationship⁷

$$\frac{\sum_{\Delta\nu} q_{v'}, q_{v''}}{N} = \frac{3hc}{8\pi^2 e^2} \frac{\Delta\nu}{\nu} \frac{k_{av}}{R_e^2 n_0 N} = \frac{3hc}{8\pi^2 e^2} \frac{\rho_v}{\nu} \frac{k_{av}}{R_e^2 n_0},$$

where N is the number of vibrational bands in the interval $\nu \pm (\Delta\nu/2)$; $\rho_v = w''/p$ is the average distance between vibrational bands; p is the number of excited vibrational levels of the lower state [the summation is carried out over all transitions (v', v'') whose wave numbers fall in the interval of averaging, $\nu \pm (\Delta\nu/2)$]. Collecting all terms, we obtain finally

$$(k_{0\max})_{av} = 2 \sqrt{\frac{2 \ln 2}{\pi e}} \sqrt{\frac{B''}{kT}} \frac{\omega''}{\Delta_D} \frac{k_{av}}{p\eta} \approx 0.803 \sqrt{\frac{B''}{kT}} \frac{\omega''}{\Delta_D} \frac{k_{av}}{p\eta}. \quad (9)$$

The uncertainty in the definition of p may be avoided in a more precise calculation by separating k_{av} into components, each of which corresponds to transitions

from a group p' of lower vibrational levels. According to (8), the choice of p' influences the final result only slightly. In particular, for $p' = 1$ we get

$$\frac{k_{av}^{(e)}}{k_{av}} = \sum_{p'=0}^{\infty} w_{p'} F^{(e)} [(k_{0\max})_{av} l w_{p'}],$$

where $(k_{0\max})_{av}$ is determined by formula (9) with $p = 1$.

COMPARISON OF DIFFERENT MODELS

For the model of random distribution of lines of equal intensity $k_{0\max}$,

$$w(k_0) = \delta(k_0 - k_{0\max}),$$

where δ is the delta function, we obtain² from (6) and (7)

$$F_{\text{equal}} = \frac{k_{av}^{(e)}}{k_{av}} = \frac{\zeta(a, k_{0\max} l)}{\sqrt{\pi} k_{0\max} l}.$$

In applying the model with a Boltzmann intensity distribution or the equal-intensity model to a real spectrum, one must evidently consider the quantities k_{av} to be the same in both cases. However, in the choice of the values of $k_{0\max}$ in one model or the other there is a certain arbitrariness, which is associated with the noncorrespondence of the real spectrum with the models applied. We have given above the rule for determining $(k_{0\max})_{av}$ in the Boltzmann model (we shall designate association with this model by the index "B"). But if the lines have nonidentical intensities ranging on the average from $(k_{0\max})_{av}^B$ to 0 and we attempt to represent such a spectrum as a set of lines of equal intensity $k_{0\max}$ and of finite crowding with the average interval ρ , then we shall consider as one of the natural assumptions

$$k_{0\max} = \frac{1}{2} (k_{0\max})_{av}^B.$$

Knowing k_{av} , one can then find ρ in the equal-intensity model, which was generally not possible in the Boltzmann model. Comparison of the asymptotic expressions for F in one model and the other shows that, with a somewhat different ratio,

$$k_{0\max} = \frac{(k_{0\max})_{av}^B}{1.85}$$

both models give the same result in both the linear region and the square root region, and in the intermediate region the difference is insignificant (see Table 3).

Table 3. Comparison of the Boltzmann, Equal-Intensity, and Exponential Models

α	$\pm \sqrt{\pi} k_{0\max} \cdot l$	$1-1$	1	10	1'	1''	1'''	1''''	1'''''
0	$F_B(1.85x)$	9.6 ⁻¹	6.7 ⁻¹	1.80 ⁻¹	2.7 ⁻²	3.8 ⁻³	4.7 ⁻⁴	5.6 ⁻⁵	6.6 ⁻⁶
	$F_{eq}(x)$	9.6 ⁻¹	7.3 ⁻¹	1.85 ⁻¹	2.5 ⁻²	3.0 ⁻³	3.5 ⁻⁴	3.8 ⁻⁵	4.2 ⁻⁶
	$F_{ex}(0.785x)$	9.4 ⁻¹	6.5 ⁻¹	1.85 ⁻¹	2.7 ⁻²	3.3 ⁻³	3.8 ⁻⁴	4.3 ⁻⁵	4.7 ⁻⁶
1	$F_B(1.85x)$	1.00	8.4 ⁻¹	4.2 ⁻¹	1.45 ⁻¹	4.7 ⁻²	1.45 ⁻²	—	—
	$F_{eq}(x)$	9.8 ⁻¹	8.8 ⁻¹	4.5 ⁻¹	1.45 ⁻¹	4.6 ⁻²	1.45 ⁻²	—	—
	$F_{ex}(0.785x)$	1.00	8.4 ⁻¹	4.2 ⁻¹	1.40 ⁻¹	4.5 ⁻²	1.45 ⁻²	—	—
100	$F_B(1.85x)$	1.00	1.00	1.00	8.4 ⁻¹	4.3 ⁻¹	1.45 ⁻¹	—	—
	$F_{eq}(x)$	1.00	1.00	1.00	9.0 ⁻¹	4.6 ⁻¹	1.45 ⁻¹	—	—
	$F_{ex}(0.785x)$	1.00	1.00	1.00	8.3 ⁻¹	4.3 ⁻¹	1.45 ⁻¹	—	—

Note: See note to Table 1.

A consequence of the exponential distribution (1) for lines with a dispersion contour is the formula¹⁻³

$$F_{\text{expon.}} = \frac{1}{\sqrt{1 + (k_0^L)_{\text{av.}}^2}}, \quad (10)$$

in which the average absorption coefficient at the maximum of the line is connected with the average distance between lines by the relation

$$(k_0^L)_{\text{av.}} = \frac{2}{\pi} \frac{\rho}{\Delta\sigma} k_{\text{av.}}$$

Since, however, in the general case of rotational lines of Lorenz-Doppler shape, we apply the distribution (1) not to the parameter k_0^L but to k_0 (i.e., to the absorption coefficient at the maximum for a Doppler line shape), we find an asymptotic value for $F_{\text{expon.}}$ with the help of (6) and (7):

$$F_{\text{expon.}}^{\text{av.}} = \sqrt{\frac{a \sqrt{\pi}}{l (k_0)_{\text{expon.}}^{\text{av.}}}}, \quad (11)$$

where $(k_0)_{\text{expon.}}^{\text{av.}}$ is the average absorption coefficient k_0 for an exponential intensity distribution. Comparing (11) with the asymptotic value of F in the case of equally intense lines, we find the condition for agreement with F_{max} of the equal-intensity model² to be

$$k_{0 \text{ max}} = \frac{4}{\pi} (k_0)_{\text{expon.}}^{\text{av.}}$$

In Table 3, a comparison is presented with the values of $F_{\text{expon.}}$ obtained by numerical integration, showing the slight dependence of the ratio $k_{\text{av.}}^{\text{meas.}}/k_{\text{av.}}$ on the character of the intensity distribution.

REFERENCES

1. R. Goody, Quart. J. Roy. Meteorol. Soc. **78**, 165 (1952).
2. G. Plass, J. Opt. Soc. Am. **48**, 690 (1958).
3. B. Kivel, H. Mayer, and H. Bethe. Ann. Physik. **2**, 57 (1957).
4. A. Mitchell and M. Zemansky, Resonance Radiated and Excited Atoms, Ob'ed. Nauch. i Tekh. Izd., Moscow, Leningrad, 1937; Cambridge Univ. Press 1934.
5. S. Penner and R. Kavanagh, J. Opt. Soc. Am. **43**, 385 (1953).
6. G. Herzberg, "Spektry i stroenie dvukhatomnykh molekul" (Spectra and Structure of Diatomic Molecules). Izd. Inostrannoi Lit., Moscow, 1949. Translation of Molecular Spectra and Molecular Structures I. Spectra of Diatomic Molecules, 2nd ed., Van Nostrand, New York, 1950.
7. V. Soshnikov, Uspekhi Fiz. Nauk **74**, No. 1 (1961).

VIBRATIONAL SPECTRA OF AROMATIC COMPOUNDS

X. Calculation and Interpretation of the Vibrational Spectra of Pyridine and the Deuteriopyridines. Nonplanar Vibrations

M. A. Kovner, Yu. S. Korostelev, and V. I. Berezin (pp. 457-465)

Received 16 May 1960

A calculation of the values of the fundamental nonplanar vibration frequencies has been completed for the molecules of pyridine and a series of its deuterium derivatives: 4- $\text{C}_5\text{H}_4\text{DN}$; 2,6- $\text{C}_5\text{H}_3\text{D}_2\text{N}$; 3,5- $\text{C}_5\text{H}_3\text{D}_2\text{N}$; 2- $\text{C}_5\text{H}_4\text{DN}$; 3- $\text{C}_5\text{H}_4\text{DN}$; $\text{C}_5\text{D}_5\text{N}$. It is shown that the results of the calculation are in good agreement with the experimental data on the vibrational spectra of the substances listed, and also with the product and sum rules. A set of force constants and interaction coefficients corresponding to the nonplanar vibrations of the pyridine and deuterated pyridine molecules is established.

The Raman and infrared spectra of pyridine have been investigated not less than 25 times. However, up to now there has been no interpretation of these spectra which was founded on a theoretical calculation of all the fundamental vibration frequencies of the molecules of pyridine and the deuteriopyridines, a fact which is apparently associated with the difficulties in determining the force constants from high-order secular equations. On this basis, such a calculation seems very timely, and the availability of sufficiently complete experimental data on the vibrational spectra of the deuteriopyridines makes it entirely feasible. In the present work, an attempt has been undertaken at overcoming the difficulties referred to, the first part being devoted to the nonplanar vibrations. A prerequisite for the calculation is the establishment of the geometrical parameters of the pyridine molecule.

1. GEOMETRY OF THE PYRIDINE MOLECULE

The replacement of one carbon atom by a nitrogen atom in the benzene ring entails changes in all the bond lengths and valence angles. Of the 15 different quantities which characterize the geometrical structure of the molecule, 10 are independent. The determination of these quantities has been carried out by many authors (Table 1). In refs. 1 and 5, only the average values of the bond lengths and approximate values of certain angles were determined. In refs. 2 and 3, only the values for the moments of inertia of $\text{C}_5\text{H}_5\text{N}$ were used; these do not unequivocally determine the bond lengths and the angles between them. In ref. 4, the moments of inertia of pyridine and its deuterium derivatives were used, and, with an arbitrary choice of the CH bond lengths, the remaining seven parameters were determined. The arbitrariness

of the choice of the CH bond lengths was eliminated in ref. 7, in which, to determine all ten parameters, quantum-mechanical relationships connecting the bond lengths with the hybridization parameter in the wave functions of the carbon atom were introduced.⁶ Since ref. 7 is the only work known to us in which all ten parameters are determined, we have taken the data of this work for our calculation (last column of Table 1).

Table 1. Bond Lengths (in Å) and Valence Angles in the Pyridine Molecule According to the Data of Various Authors

Bonds and angles	Method					
	Electron diffraction ¹	Microwave spectrum ²	Microwave spectrum ³	Microwave spectrum ⁴	Electron diffraction ⁵	Calculation ⁷
C ₂ -H ₂	1.090	1.080	1.080	1.085	1.078	1.092
C ₃ -H ₃	1.090	1.080	1.080	1.080	1.078	1.080
C ₄ -H ₄	1.090	1.080	1.080	1.075	1.078	1.080
N-C ₅	1.370	1.350	1.355	1.342	1.377	1.355
C ₂ -C ₃	1.405	1.390	1.390	1.391	1.377	1.378
C ₃ -C ₄	1.405	1.390	1.390	1.398	1.377	1.397
C ₅ NC ₂	119°	117°	115°30'	116°42'	—	116°46'
NC ₂ C ₃	121°	123°	—	118°36'	—	125°04'
C ₅ C ₄ C ₃	121°	119°48'	—	118°06'	—	118°23'
C ₅ C ₄ C ₆	121°	117°24'	—	115°44'	—	114°18'
NC ₂ H ₂	—	—	—	120°18'	—	120°38'
C ₅ C ₄ H ₂	—	—	—	120°17'	—	120°30'
C ₅ C ₄ H ₃	—	—	—	121°07'	—	121°07'
C ₅ C ₄ H ₄	—	—	—	120°57'	—	120°50'

2. SYMMETRY COORDINATES

The molecules of C₅H₅N, 4-d-, 2,6-d₂-, and 3,5-d₂-pyridine, and C₅D₅N belong to the symmetry group C_{2v}; the molecules of 2-d- and 3-d-pyridine belong to C_s. The eight nonplanar vibrations of each molecule belong to the symmetry types A₂ (three vibrations), B₂ (five vibrations), and A'' (eight vibrations).

The symmetry coordinates of types A₂ and B₂ have the form

A₂:

$$R_1 = \frac{2}{\sqrt{2}}(\rho_2 - \rho_6); \quad R_2 = \frac{1}{\sqrt{2}}(\rho_3 - \rho_5);$$

$$K_1 = \frac{1}{\sqrt{2}}(\kappa_{23} + \kappa_{56}); \quad K_2 = \frac{1}{\sqrt{2}}(\kappa_{34} + \kappa_{45}); \quad K_3 = \frac{1}{\sqrt{2}}(\kappa_{12} + \kappa_{61});$$

B₂:

$$R_1 = \frac{1}{\sqrt{2}}(\rho_2 + \rho_6); \quad R_2 = \frac{1}{\sqrt{2}}(\rho_3 + \rho_5); \quad R_3 = \rho_4;$$

$$K_1 = \frac{1}{\sqrt{2}}(\kappa_{23} - \kappa_{56}); \quad K_2 = \frac{1}{\sqrt{2}}(\kappa_{34} - \kappa_{45}); \quad K_3 = \frac{1}{\sqrt{2}}(\kappa_{12} - \kappa_{61}).$$

In the case of A'', these same coordinates were used as approximate symmetry coordinates. Coordinates of types ρ and κ describe the bending of the CH bonds out of the plane of the ring and the bending of the CC or CN bonds out of the plane of two adjacent ring bonds.

The symmetry coordinates given above satisfy the additional relations

$$A_2: K_2 + MK_1 = 0; \quad K_3 + NK_1 = 0;$$

$$B_2: K_1 + SK_2 + TK_3 = 0.$$

The first of the coordinates entering into these relations were excluded. It follows from the geometrical parameters taken for the calculation that M = 0.4574, N = 0.5171, S = 0.5130, T = 0.5395. If the hexagon were regular, then M, N, S, and T would equal 0.5.

3. KINEMATIC COEFFICIENTS IN SYMMETRY COORDINATES

For the calculation of the kinematic coefficients (k. c.), the method of ref. 8 was applied, but without the approximate allowance for anharmonicity by means of the introduction of "spectroscopic" masses. The following values for the dimensionless masses and bond lengths were used in the calculation (1.09 Å was taken as the unit of length⁸): $\epsilon_H = 1$, $\epsilon_D = 0.5003$, $\epsilon_C = 0.0839$, $\epsilon_N = 0.0719$, $\sigma_{C_2-H} = 0.9982$, $\sigma_{C_3-H} = \sigma_{C_4-H} = 1.0092$, $\sigma_{N-C_2} = 0.8044$, $\sigma_{C_2-C_3} = 0.7910$, $\sigma_{C_3-C_4} = 0.7802$.

The calculated values of the k. c. for C₅H₅N in symmetry coordinates are presented in Table 2. Only the values of certain diagonal k. c. of the deuteriopyridines differ from the values of Table 2, namely:

$$4-d \cdot B_2: (R_3, R_3) 1.1454;$$

$$2,6-d_2 \cdot A_2: (R_1, R_1) 1.1873, \quad B_2: (R_1, R_1) 1.2903;$$

$$3,5-d_2 \cdot A_2: (R_2, R_2) 1.1028, \quad B_2: (R_2, R_2) 1.2008;$$

$$C_5D_5N \cdot A_2: (R_1, R_1) 1.1873, (R_2, R_2) 1.1028, \quad B_2: (R_1, R_1) 1.2903;$$

$$(R_2, R_2) 1.2008; \quad (R_3, R_3) 1.1454;$$

$$2-d \cdot A_2: (R_1, R_1) 1.4362, \quad B_2: (R_1, R_1) 1.5392;$$

$$3-d \cdot A_2: (R_2, R_2) 1.3572, \quad B_2: (R_2, R_2) 1.4552.$$

In the eighth-order k. c. matrices, in addition, there appear the k. c. for the interaction between the A₂ and B₂ symmetry coordinates: (R₁(A₂), R₁(B₂)) - 0.2489 in the case of the 2-d compound, and (R₂(A₂), R₂(B₂)) - 0.2544 in the case of 3-d.

Table 2. Kinematic Coefficients and Force Constants (in units of 10⁶ cm⁻²) of the Pyridine Molecule in Symmetry Coordinates

Symmetry type	Interacting coordinates	Kinematic coefficients	Force constants
A ₂	R ₁ , R ₁	1.6851	0.6439
	R ₁ , R ₂	-0.3643	-0.0541
	R ₁ , K ₁	0.5882	-0.2907
	R ₂ , R ₂	1.8117	0.6982
	R ₂ , K ₁	-0.5264	0.3988
	K ₁ , K ₁	0.6180	0.5752
B ₂	R ₁ , R ₁	1.7881	0.5717
	R ₁ , R ₂	-0.3643	-0.0266
	R ₁ , R ₃	0.0796	-0.0537
	R ₁ , A ₂	-0.4002	0.0827
	R ₁ , K ₃	-0.9313	0.3055
	R ₂ , R ₂	1.7097	0.5487
	R ₂ , R ₃	-0.4598	-0.0766
	R ₂ , A ₂	0.8413	-0.2864
	R ₂ , K ₃	0.3867	-0.0830
	K ₁ , R ₃	1.6344	0.6087
	K ₁ , K ₂	-0.7574	0.2690
	K ₁ , K ₃	-0.0874	-0.0274
	K ₂ , K ₂	1.1499	0.5108
	K ₂ , K ₃	0.42 8	0.1282
	K ₃ , K ₃	1.2092	0.5896

4. DISCUSSION OF THE EXPERIMENTAL FREQUENCY VALUES FOR NONPLANAR VIBRATIONS AND THEIR ASSIGNMENT TO THE SYMMETRY TYPES

For the calculation of the force constants, it is necessary first to establish the most probable set of fundamental frequencies of the nonplanar vibrations of pyridine and the deuteriopyridines. In Table 3 are collected the frequency assignments proposed by various authors,

among which are large discrepancies. It has been shown in ref. 11 that the set of pyridine frequencies of symmetry type B_2 from ref. 10 does not lead to good agreement of the calculated and experimental values of the thermodynamic functions. To this it should be added that calculations carried out by us before the appearance of ref. 11 and based on the set of B_2 frequencies for C_5H_5N and C_5D_5N from ref. 10 led to discordant equations relative to the force constants. Hence it follows that the product rule, which all the frequency sets of Table 3 satisfy, can serve only as a necessary but not as a sufficient criterion for the accuracy of these sets. A further test of them can be based on the sum rules,^{13,14} which, taking account of the breakdown into symmetry types, have the following form:

$$A_2, B_2: \Delta_1(\nu^2) = 2 \sum \nu^2 (C_5H_5N) + \sum \nu^2 (C_5D_5N)$$

$$- [\sum \nu^2 (4-d) + \sum \nu^2 (2,6-d_2) + \sum \nu^2 (3,5-d_2)] = 0.$$

$$A'': \Delta_2(\nu^2) = 2 \sum \nu^2 (2-d) - [\sum \nu^2 (C_5H_5N) + \sum \nu^2 (2,6-d_2)] = 0,$$

$$\Delta_3(\nu^2) = 2 \sum \nu^2 (3-d) - [\sum \nu^2 (C_5H_5N) + \sum \nu^2 (3,5-d_2)] = 0.$$

Table 3. Fundamental Frequency Values (cm^{-1}) of the Nonplanar Vibrations of Pyridine and the Deuteriopyridines According to the Data of Various Authors

Molecule	C_5H_5N			4-d		2,6-d ₂		3,5-d ₂		C_5D_5N		2-d	3-d
	N	[¹]	[²]	[³]	[⁴]	[⁵]	[⁶]	[⁷]	[⁸]	[⁹]	[¹⁰]	[¹¹]	[¹²]
40a	747	886	886	890	889	765	867	690	690	814	823		
16a	404	374	374	365	373	340	352	329	329	360	350		
17a	1061	981	981	968	979	926	784	798	798	970	965		
4	652	675	749	665	743	743	713	625	567	665	670		
5	941	942	942	834	862	889	918	762	823	901	902		
10a	710	749	886	743	862	839	897	567	762	748	717		
11	669	703	700	633	625	586	585	530	530	638	632		
16e	374	405	405	383	381	397	391	371	371	405	404		

These rules must also be fulfilled for the frequencies themselves, i.e., for $\Delta(\nu)$. For the A_2 frequencies from ref. 11, $\Delta_1(\nu^2) = 0.0598 \times 10^6 \text{ cm}^{-2}$ and $\Delta_1(\nu) = 24 \text{ cm}^{-1}$. For a symmetry type which includes only three frequencies in all, these values are too large. For the A'' frequencies from refs. 11 and 12, $\Delta_2(\nu^2) = -0.6450 \times 10^6 \text{ cm}^{-2}$; $\Delta_3(\nu^2) = -0.7753 \times 10^6 \text{ cm}^{-2}$; $\Delta_2(\nu) = -406 \text{ cm}^{-1}$ and $\Delta_3(\nu) = -504 \text{ cm}^{-1}$. These figures clearly show the incorrectness of the interpretation proposed in refs. 11 and 12 for the partially deuterated pyridines. Therefore, we selected the C_5H_5N and C_5D_5N frequencies proposed in ref. 11 as initial frequencies. The frequency values for the other deuteriopyridines were determined by the preliminary calculation described below.

5. METHOD AND RESULTS OF THE FORCE CONSTANT CALCULATION

The force constants in symmetry coordinates (21 of them) are the following linear combinations of the 36 force constants in internal vibrational coordinates (their symbols are clear from Table 4 and the Figure and correspond to the symbols in ref. 15 for the force constants of benzene).

$$A_2: (R_1, R_1) = A_1 - a''_m; (R_1, R_2) = a'_0 - a'_p;$$

$$(R_1, K_1) = c'_0 - c'_p - M(c'_m + c'_p) + N(c''_0 + c''_m);$$

$$(R_2, R_2) = A_2 - a''_m;$$

Table 4. Symbols for the Force Constants of the Internal Vibrational Coordinates (see Figure)

	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	x_{23}	x_{34}	x_{45}	x_{56}	x_{61}	x_{12}
ρ_2	A_1	a'_0	a'_m	a'_p	a'_m	c'_0	c'_m	c'_p	$-c'_p$	$-c'_m$	$-c'_0$
ρ_3		A_2	a''_0	a''_m	a''_p	$-c''_0$	c''_m	c''_p	$-c''_p$	$-c''_m$	$-c''_0$
ρ_4			A_3	a''_0	a''_m	$-c''_0$	$-c''_m$	c''_p	c''_p	$-c''_p$	$-c''_p$
ρ_5				A_2	a'_0	$-c'_0$	$-c'_m$	$-c'_0$	c'_p	c'_p	$-c'_p$
ρ_6					A_1	$-c'_0$	$-c'_m$	$-c'_0$	c'_p	c'_p	$-c'_p$
x_{23}						B_2	b'_0	b'_m	b'_p	b'_m	b'_0
x_{34}							B_3	b'_0	b'_m	b'_p	b'_m
x_{45}								B_3	b'_0	b'_m	b'_p
x_{56}									B_2	b'_0	b'_m
x_{61}										B_1	b'_0
x_{12}											B_1

$$(R_2, K_1) = -c''_0 + c''_p - M(c''_0 + c''_m) + N(c''_0 + c''_p);$$

$$(K_1, K_1) = B_2 + b''_p - 2M(b''_0 + b''_m) + M^2(B_3 + b''_0) - 2N(b''_0 + b''_m) + 2MN(b''_m + b''_p) + N(B_1 + b''_0);$$

B_2 :

$$(R_1, R_1) = A_1 + a''_m; (R_1, R_2) = a'_0 + a'_p; (R_1, R_3) = \sqrt{2} a'_m;$$

$$(R_1, K_2) = c'_m - c'_p - S(c'_0 + c''_p);$$

$$(R_1, K_3) = -c''_0 + c''_m - T(c'_0 + c''_p); (R_2, R_2) = A_2 + a''_m;$$

$$(R_2, R_3) = \sqrt{2} a''_0; (R_2, K_2) = c''_0 - c''_m + S(c''_0 + c''_p);$$

$$(R_2, K_3) = -c''_m + c''_p + T(c''_0 + c''_p);$$

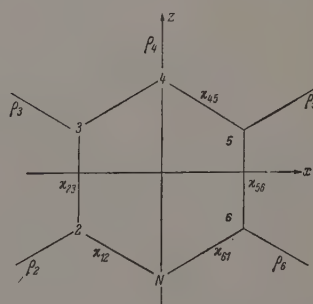
$$(R_3, R_3) = A_3; (R_3, K_2) = -\sqrt{2} c''_0 + S\sqrt{2} c''_m;$$

$$(R_3, K_3) = -\sqrt{2} c''_p + T\sqrt{2} c''_m;$$

$$(K_2, K_2) = B_3 - b'_0 - 2S(b''_0 - b''_m) + S^2(B_2 - b''_p);$$

$$(K_2, K_3) = b'_m - b'_p - S(b''_0 - b''_m) - T(b''_0 - b''_m) + TS(B_2 - b''_p);$$

$$(K_3, K_3) = B_1 - b'_0 - 2T(b''_0 - b''_m) + T^2(B_2 - b''_p).$$



Vibrational coordinates of the nonplanar vibrations of the pyridine molecule.

Of the six A_2 frequencies of the C_5H_5N and C_5D_5N molecules, only five are independent, as a result of which we have only five equations for the determination of the six A_2 force constants. In order to make the problem definite, we have set $A_1 - a''_m = A_2 - a''_m$. For the five force constants, a set of five equations originating in the connection between the coefficients and the roots of the secular equation was set up and strictly solved. The A_2 frequency values calculated with the help of these force constants for the 2,6-d₂ and 3,5-d₂ molecules were found

Table 5. Calculated and Observed Frequency Values (in cm^{-1}) of the Nonplanar Vibrations of Pyridine and the Deuteriopyridines

No.	Symmetry type	$\text{C}_5\text{H}_5\text{N}$		4-d		2,6- d_2		3,5- d_2		$\text{C}_5\text{D}_5\text{N}$		Symmetry type	2-d		3-d	
		$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$		$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$
10a	A_2	891	886	891	889	744	742	732	—	696	690	A''	886	—	885	—
16a	A_2	372	375	372	373	341	340	353	352	324	329	A''	380	362	380	355
17a	A_2	986	980	986	979	957	961	943	947	800	798	A''	971	970	964	965
4	B_2	744	749	734	743	744	742	706	713	578	587	A''	744	748	706	717
5	B_2	937	942	882	890	929	926	926	918	834	823	A''	932	—	929	938
10b	B_2	882	886	843	834	838	839	861	867	751	762	A''	814	814	837	823
11	B_2	705	700	623	625	555	563	587	585	522	530	A''	611	600	628	632
16b	B_2	404	405	379	371	398	397	387	391	362	371	A''	403	405	397	404

to be 347, 726, 954, and 346, 744, 936 cm^{-1} , which does not agree with the values proposed in ref. 11 (Table 3). Therefore, instead of the value 926 for the 2,6- d_2 spectrum, we chose the value 961 cm^{-1} . This weak line, explained in ref. 11 as a combination, may appear in the infrared spectrum of the liquid in violation of the selection rule. Then, in place of 765 cm^{-1} , we obtain from the product rule a frequency of the order of 740, corresponding to the superposition of lines Nos. 10a and 4. In the 3,5- d_2 spectrum, we chose in place of 784 cm^{-1} the frequency 948 cm^{-1} , whose assignment to B_1 is not confirmed by our calculation of the frequencies of the planar vibrations. Then we obtain from the product rule a frequency of the order of 730 cm^{-1} in place of 867 cm^{-1} . Taking these changes into account, we have somewhat changed the set of force constants found initially, by starting from the frequency values of all four molecules and applying the method of refining the force constants by means of a calculation of the derivatives of the frequencies with respect to the force constants.¹⁸

Using the values found for the A_2 force constants by the method just described, employing the formulas presented above for them, and going over to the leveling approximation, in which the force constants of the types ρ, ρ and ρ, κ which are equal for benzene are considered to be equal for pyridine also, we have reduced the number of unknown force constants of symmetry type B_2 from 15 to 6. The latter were found on the basis of the 10 B_2 frequencies of the $\text{C}_5\text{H}_5\text{N}$ and $\text{C}_5\text{D}_5\text{N}$ molecules and were used to calculate the frequencies of the remaining deuteriopyridines. As a result of this calculation, we have obtained the frequency assignment presented in Table 5 for the partially deuterated pyridines, which differs in a number of cases from the assignment of other authors. Then the established values of the fundamental frequencies were used for the final determination of the values of the B_2 force constants by means of a calculation of the derivatives of the frequencies with respect to the force constants (Table 2). The good agreement which is attained between the calculated and observed frequency values may serve as confirmation of the correctness of our interpretation of the spectra. It is also confirmed by the following sufficiently small values of Δ :

$$A_2: \Delta_1 (\nu^2) = -0.0371 \cdot 10^6 \text{ cm}^{-2}; \Delta_1 (\nu) = -15 \text{ cm}^{-1};$$

$$B_2: \Delta_1 (\nu^2) = 0.0128 \cdot 10^6 \text{ cm}^{-2}; \Delta_1 (\nu) = 3 \text{ cm}^{-1},$$

$$\Delta_2 (\nu^2) = 0.0055 \cdot 10^6 \text{ cm}^{-2} \quad \Delta_2 (\nu) = 7 \text{ cm}^{-1},$$

$$\Delta_3 (\nu^2) = 0.0366 \cdot 10^6 \text{ cm}^{-2} \quad \Delta_3 (\nu) = 21 \text{ cm}^{-1}.$$

The calculated and observed frequency values for all the molecules examined are tabulated in Table 5, and the formulas and numerical values of the products in Table 6.

Table 6. Formulas for the Products of the Ratios of the Deuteriopyridine Frequencies to the Pyridine Frequencies; Calculated and Experimental Values of These Products

Symmetry type	Molecules	4-d	2,6-d ₂	3,5-d ₂	C ₅ D ₅ N
	Formula and value				
A ₂	Formula	$\left(\frac{I'_x}{I_x}\right)^{\frac{1}{2}}$	$\left(\frac{m_H I'_x}{m_D I_x}\right)^{\frac{1}{2}}$	$\left(\frac{m_H I'_x}{m_D I_x}\right)^{\frac{1}{2}}$	$\frac{m_H}{m_D} \left(\frac{I'_x}{I_x}\right)^{\frac{1}{2}}$
	Π _{calc.}	1.000	0.742	0.745	0.551
	Π _{exptl.}	0.997	0.744	0.749	0.556
B ₂	Formula	$\left(\frac{m_H M' I'_x}{m_D M I_x}\right)^{\frac{1}{2}}$	$\left(\frac{m_H M' I'_x}{m_D M I_x}\right)^{\frac{1}{2}}$	$\left(\frac{m_H M' I'_x}{m_D M I_x}\right)^{\frac{1}{2}}$	$\left(\frac{m_H^3 M' I'_x}{m_D^3 M I_x}\right)^{\frac{1}{2}}$
	Π _{calc.}	0.737	0.728	0.728	0.390
	Π _{exptl.}	0.741	0.727	0.732	0.394
Symmetry type	Molecules	2-d	3-d		
	Formula and value				
A''	Formula	$\left(\frac{m_H M' I'_x I'_x}{m_D M I_x I_x}\right)^{\frac{1}{2}}$			
	Π _{calc.}	0.736	0.737		
	Π _{exptl.}	0.741	0.744		

Note: $\Pi = \frac{\nu_i (\text{C}_5\text{H}_5\text{D}_{2-3}\text{N})}{\nu_i (\text{C}_5\text{H}_5\text{N})}$; M — mass of the entire molecule; I — moments of inertia; the prime refers to the heavier molecule.

6. FORCE FIELD OF THE PYRIDINE MOLECULE

By inverting the force constant matrix and using the additional relationships between the coordinates, we have computed a complete set of interaction coefficients in the internal vibrational coordinates. In Table 7, they are compared with the interaction coefficients of benzene, computed by us according to the data of ref. 15. From this table, Table 4, and the Figure, the following conclusions may be drawn concerning the effect on the force field of the replacement of one carbon atom by a nitrogen atom.

1. In correspondence with the breakdown of the equivalence of the bonds, interaction coefficients which are the same in the benzene molecule are not the same in pyridine.

2. The diagonal interaction coefficients of the CH bonds change insignificantly. At the same time, the interaction of CH bonds in the ortho-positions is strengthened; the interaction of CH bonds in the meta-positions, separated by the nitrogen atom, is somewhat weakened.

Table 7. Comparison of the Values of the Interaction Coefficients of Benzene and Pyridine

Symbols for the interaction coefficients (see Table 4 and Figure)	Benzene ¹⁵		Pyridine		
	10 ⁻⁵ cm/dyne	10 ⁻⁶ cm ²	10 ⁻⁶ cm ²		
$(A_1)^{-1}, (A_2)^{-1}, (A_3)^{-1}$	3.7867	2.2330	2.3038; 2.4039; 2.3204		
$(a_0')^{-1}, (a_0'')^{-1}$	-0.3292	-0.1941	-0.3667; -0.3197		
$(a_m')^{-1}, (a_m'')^{-1}, (a_m''')^{-1}$	0.3236	0.1908	0.2205; 0.1725; 0.2744		
$(a_p)^{-1}$	0.1927	0.1136	0.1371		
$(c_0')^{-1}, (c_0'')^{-1}, (c_0''')^{-1}, (c_0^{IV})^{-1}, (c_0^V)^{-1}$	2.1663	1.2775	1.1183; 0.9641; 1.2348; 1.2213; 1.1155		
$(c_m')^{-1}, (c_m'')^{-1}, (c_m''')^{-1}, (c_m^{IV})^{-1}, (c_m^V)^{-1}$	-1.0379	-0.6120	-0.5144; -0.2533; -0.5294; -0.4457; -0.4914		
$(c_p')^{-1}, (c_p'')^{-1}, (c_p''')^{-1}, (c_p^{IV})^{-1}, (c_p^V)^{-1}$	-0.0905	-0.0534	-0.1142; -0.2562; -0.2777; -0.3364; -0.1499		
$(B_1)^{-1}, (B_2)^{-1}, (B_3)^{-1}$	5.5413	3.2677	1.6672; 2.4154; 2.3193		
$(b_0')^{-1}, (b_0'')^{-1}, (b_0''')^{-1}, (b_0^{IV})^{-1}$	-3.8407	-2.2649	-0.7777; -1.4060; -1.6526; -1.6233		
$(b_m')^{-1}, (b_m'')^{-1}, (b_m''')^{-1}$	0.4395	0.2592	0.1720; -0.3141; 0.1310		
$(b_p')^{-1}, (b_p'')^{-1}$	1.2611	0.7437	0.6148; 0.9113		

3. The interaction of the CH and CN bonds is weakened in comparison with the corresponding interaction of the CH and CC bonds in benzene.

4. The diagonal interaction coefficient of the CN bonds is significantly less than the corresponding coefficient in benzene.

5. The interaction of the CN and CC bonds and of the CC bonds among themselves is fundamentally weakened, which may easily be explained qualitatively by the greater degree of localization of the π -electrons in the pyridine ring.

E. E. Kolosov participated in this research.

REFERENCES

1. V. Schomaker and L. Pauling, *J. Am. Chem. Soc.* **61**, 1769 (1939).
2. K. E. McCulloh and G. F. Pollnow, *J. Chem. Phys.* **22**, 681 (1954).
3. B. B. DeMoore, W. S. Wilcox, and J. H. Goldstein, *J. Chem. Phys.* **22**, 876 (1954).
4. B. Bäk, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.* **22**, 2013 (1954).
5. A. Almenningen, O. Bastiansen, and L. Hansen, *Acta Chem. Scand.* **9**, 1306 (1955).
6. C. W. N. Cumper, *Trans. Faraday Soc.* **54**, 1261 (1958).
7. C. W. N. Cumper, *Trans. Faraday Soc.* **54**, 1266 (1958).
8. M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, "Kolebaniya molekul" (Molecular Vibrations). Gosudarst. Izd. Tekh.-Teoret. Lit., Moscow, Leningrad, 1949.
9. C. H. Kline and J. Turkevich, *J. Chem. Phys.* **12**, 300 (1944).
10. L. Corsin, B. J. Fax, and R. C. Lord, *J. Chem. Phys.* **21**, 1170 (1953).
11. J. K. Wilmhurst and H. J. Bernstein, *Can. J. Chem.* **35**, 1183 (1957).
12. F. A. Andersen, B. Bäk, S. Brodersen, and J. Rastrup-Andersen, *J. Chem. Phys.* **26**, 1047 (1955).
13. L. M. Sverdlov, *Doklady Akad. Nauk SSSR* **78**, 1115 (1951).
14. L. M. Sverdlov, *Doklady Akad. Nauk SSSR* **94**, 451 (1954).
15. F. A. Miller and B. L. Crawford, *J. Chem. Phys.* **14**, 282 (1946).
16. L. S. Mayants, *Opt. i Spektr.* **5**, 378 (1958).

INFLUENCE OF SOLVENT VISCOSITY ON THE FLUORESCENCE SPECTRA OF CERTAIN ORGANIC COMPOUNDS

A. S. Cherkasov and G. I. Dragneva (pp. 466-472)

Received 2 June 1960

We have studied the influence of the change in solvent viscosity with a change in temperature on the position and shape of the fluorescence spectra of solutions of 2-acetylanthracene and 3-aminophthalimide. We have established the presence of sharp differences between the temperature dependences of the positions of the maxima in the fluorescence spectra and those of the static dielectric constant of the solvent. For solutions of 2-acetylanthracene in the butyl alcohols, we observed, as the temperature was lowered, the appearance of a spectrum with fine structure (characteristic for temperatures of -183 and -196°C) against the background of a continuous spectrum (characteristic for high temperatures). The experimental facts obtained are interpreted on the basis of the concept that, in the systems studied, the influence of the solvent on the spectra is fundamentally determined by the interaction between excited molecules of the fluorescing substance and solvent molecules oriented in a definite way relative to them during the lifetime of the excited state.

In a number of works devoted to attempts at constructing a theory of the influence of the medium on the position of the absorption and radiation spectra of organic compounds,* the action of the solvent has been

*A survey of the literature on this question is given in ref. 1.

linked with its macroscopic characteristics—its static dielectric constant ϵ and its refractive index n . However, although a definite link between these quantities has indeed been observed in a number of cases, an unequivocal experimental confirmation of the accuracy of these theories is lacking. This is associated in particular with the fact that it is difficult to separate the influence of the solvent as a medium with certain macroscopic properties from the influence of the molecules of the solvent directly surrounding the dissolved molecule, which may also prove to be controlling. The latter must not be neglected, since the formation in solution of molecular compounds (of one or another degree of stability) between the most varied compounds, the formation of solvate envelopes around dissolved molecules, is an altogether definitely established fact.

To clarify how the orientation of the solvent around the dissolved molecule influences the spectrum, we may make use of the following circumstance. It is well known that, in many cases, the influence of the solvent on the fluorescence spectrum differs from its influence on the absorption spectrum, which is associated with a difference in the strength of the interaction of the solvent with a dissolved molecule in the ground and the excited states. Then one may suppose that the microstructure of the solvent around the dissolved molecules (if this determines the effect on the spectrum) must change when they go over to the excited state; at the same time, the equilibrium arrangement of the solvent molecules around the excited molecules can be established only in the case where the lifetime of the excited state is greater than the time required for the rearrangement. However, the solvent viscosity affects the magnitude of the latter, and consequently, if our initial views are correct, the posi-

tion of the fluorescence spectra must also depend on the viscosity.

The disappearance of the substantial differences in the position of the fluorescence spectra in different solvents and the coming-together of the fluorescence and absorption spectra on going from room temperature to the temperature of liquid oxygen or nitrogen are well known.^{2,3} However, these facts cannot be taken as confirmation of the views presented above, since not only is the possibility of reorientation of the solvent molecules being lowered during this change, but the differences in the ϵ values almost disappear as well. It seemed to us more interesting to follow the change in the fluorescence spectrum during a gradual change of the viscosity over a wide interval, such as takes place on changing the temperature of liquids capable of glass formation. In this case, one might hope to notice a difference in the temperature dependences of the quantity ϵ and of the position of the fluorescence spectrum, since, if the latter is governed by the reorientation of solvent molecules around excited molecules of the dissolved substance (during the lifetime of the excited state, which equals approximately 10^{-8} sec), then the solvent must become "solid" toward such a reorientation at lower viscosity values than it will toward the dipole orientation, unlimited in time, which fundamentally determines the value of the static dielectric constant (ϵ_{stat}) of polar liquids.

As such solvents, we have used glucose, glycerol, ethylene glycol, and *n*-butyl and isobutyl alcohols, previously purified by recrystallization (glucose) or by distillation through a fractionating column (the other solvents). 2-Acetylanthracene and 3-aminophthalimide were the objects of investigation. The fluorescence spectra were measured with the help of a UM-2 monochromator with a photoelectric attachment. The spectral sensitivity of the apparatus (in relative number of quanta per unit of frequency interval) was determined on the basis of a source with a known energy distribution over the spectrum.

The positions of the fluorescence spectra of 2-acetylanthracene^{4,5} and 3-aminophthalimide^{6,7} depend very

strongly on the solvent used. The spectral maxima shift toward lower frequencies by 4000-5000 cm^{-1} on going from nonpolar solvents of the saturated-hydrocarbon type to alcohols and water.* At the same time, the position of

As has been shown in refs. 4 and 5, hydroxyl-containing solvents show the strongest influence on the fluorescence spectrum of 2-acetylanthracene. From a study of the changes in the spectra and in the fluorescence yields⁹ in solvent mixtures, there follows the necessity of recognizing the presence of close-order interactions between the hydroxyl groups of the solvent and the excited acetylanthracene molecules, resulting, evidently, in the formation of hydrogen bonds.

The absorption spectra is either almost entirely unchanged (2-acetylanthracene) or changed considerably less (3-aminophthalimide). On raising the temperature of solutions of 3-aminophthalimide in alcohols of the aliphatic series from -60 to +80°C, an insignificant (400 cm^{-1}) shift of the absorption spectrum to longer wavelengths was observed, and there was no shift in the fluorescence spectrum.⁶ However, heating of a glycerol solution of 3-aminophthalimide from 20 to 270°C leads to a pronounced shift (400 cm^{-1}) in the fluorescence spectrum also, but in the opposite direction (with respect to the shift in the absorption spectrum).⁸

We have investigated in detail the fluorescence spectra of solutions of 2-acetylanthracene in glucose,⁵ glycerol, ethylene glycol, and *n*-butyl and isobutyl alcohols, as well as solutions of 3-aminophthalimide in glycerol and isobutyl alcohol, over a wide temperature interval, which has enabled us to uncover a number of substantial peculiarities, not previously noticed, in the shift in the maxima of the fluorescence bands as a function of temperature.

The fluorescence spectra of 2-acetylanthracene obtained at various solution temperatures are represented in Fig. 1.

As can be seen from the figure, the fluorescence spectra of 2-acetylanthracene in glycerol and ethylene glycol remain smooth over the entire temperature interval investigated, and only a certain broadening is observed in them as the temperature is raised. The spectra of 2-acetylanthracene in glucose and of 3-aminophthalimide in glycerol and isobutyl alcohol, which are not shown here, are also of an analogous character.

An entirely different picture is observed for solutions of 2-acetylanthracene in *n*-butyl and isobutyl alcohols (Fig. 1, c, d). In this case the fluorescence spectrum, smooth at room temperature, acquires a fine structure as the temperature is lowered to the boiling point of liquid nitrogen (or oxygen). The vibrational structure has a characteristic "anthracenic" appearance, and the spectra are very similar to the fluorescence spectra of solutions of 2-acetylanthracene in such inert solvents as the saturated hydrocarbons. Thus the butyl alcohols, at low temperatures, prove to be analogous to inert solvents with respect to their influence on fluorescence spectra, while in the case of ethylene glycol, glycerol, and glucose a stronger interaction with the excited acetylanthracene molecules takes place, which manifests itself in the retention of the "washed-out" form of the spectra even at low temperatures.

This difference in the spectra may be explained if we start from the viewpoint already enunciated that the influence of hydroxyl-containing solvents is fundamentally determined by an interaction of the hydroxyl groups with

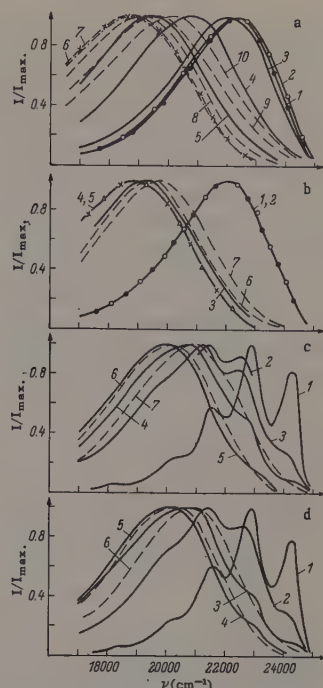


Fig. 1. Fluorescence spectra of solutions of 2-acetylanthracene at various temperatures (°C). a—Solvent: glycerol. Temperature (single arabic numbers refer to curves): 1—(-183); 2—(-90); 3—(-60); 4—(-25); 5—(-8); 6—(+25); 7—(+52); 8—(+105); 9—(+185); 10—(+234). b—Solvent: ethylene glycol. Temperature: 1—(-183); 2—(-95); 3—(-40); 4—(-12); 5—(+20); 6—(+60); 7—(+105). c—solvent: *n*-butyl alcohol. Temperature: 1—(-183); 2—(-105); 3—(-100); 4—(-88); 5—(-55); 6—(+24); 7—(+85). d—Solvent: isobutyl alcohol. Temperature: 1—(-196); 2—(-95); 3—(-77); 4—(-55); 5—(+22); 6—(+76).

the excited acetylanthracene molecules, which manifests itself only for a fixed mutual orientation of the two. In the butyl alcohols, only one of the carbon atoms out of the four which compose the molecule has a hydroxyl group, and in solid solutions, when there is practically no possibility of movement or rotation of the molecules, the probability of a favorable arrangement of the hydroxyl groups relative to the excited molecules must be very small. This probability, however, is increased to a great extent in consequence of the increase in the relative concentration of hydroxyl groups when ethylene glycol, glycerol, or glucose is used as a solvent, since in this case each of the carbon atoms (in glucose, five of the six) which compose the molecule carries a hydroxyl group. Hence, it follows that, in solid solutions, this group of solvents must likewise show a stronger influence on the excited molecules of acetylanthracene (and consequently on the fluorescence spectra also).

If this explanation is correct, then the increase in the washed-out character of the fluorescence spectrum in solid solutions must also be observed when the lower monohydric alcohols are used as solvents instead of butyl alcohol, since in this case also the relative concentration of hydroxyl groups in a unit volume will be higher. Com-

parison of the fluorescence spectra of solutions of 2-acetylanthracene in *n*-butyl, *n*-propyl, ethyl, and methyl alcohols, obtained at -183°C , shows (Fig. 2) that this phenomenon actually takes place. While the spectra in *n*-butyl, isobutyl, and *n*-propyl alcohols show fine structure and are analogous to the spectrum in the inert solvent *n*-hexane (at room temperature), the vibrational structure is noticeably less well resolved in ethyl alcohol, and in methyl alcohol the spectrum is even more washed-out than in ethyl. At the same time, a certain shift of the spectrum to lower frequencies is also observed. We believe that the results obtained make very plausible the hypothesis set forth above concerning the causes of the difference in the fluorescence spectra at low temperatures in the solvents under consideration.

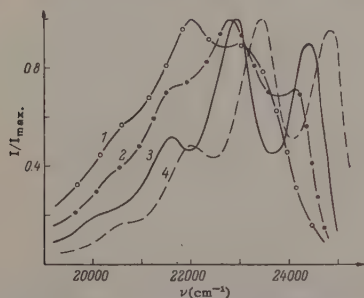


Fig. 2. Fluorescence spectra of solutions of 2-acetylanthracene at -183°C . Solvents: curve 1—methyl alcohol (96%); curve 2—ethyl alcohol (96%); curve 3—*n*-propyl alcohol; curve 4—*n*-hexane (at 20°).

The fine structure in the fluorescence spectra of solutions of 2-acetylanthracene in *n*-butyl and isobutyl alcohols begins to appear at temperatures around -50 or -60° , in the form of weak inflections in the curve on the short-wavelength side of the spectrum. On further lowering of the temperature, they manifest themselves all the more distinctly and their intensity increases (during which the intensity in the region of the shortest-wavelength inflection increases relatively more rapidly); their position is almost unchanged, remaining close to the position of the corresponding vibrational maxima in the spectrum at -183 or -190° (Fig. 1, c, d). At the same time, the spectrum as a whole shifts to a considerable extent toward shorter wavelengths. The shape of the spectra being examined and the character of their change as the temperature is changed leave no doubt that there is taking place here not the usual improvement in the resolution of the vibrational structure as the temperature is lowered, but a gradual appearance, against the background of a continuous spectrum, of another spectrum, possessing fine structure. This fact is of great interest as a clear demonstration of the presence, in solution, of different radiating centers, and the presence of reorientation of solvent molecules around an excited molecule within the lifetime of the excited state. Actually, if such a reorientation takes place, then for certain values of the viscosity the radiation of molecules around which the equilibrium orientation has not succeeded in being established will make up a significant portion of the total radiation, and the spectrum of such a radiation, as was shown above, will be analogous to the fine-structured spectrum which is characteristic for inert solvents.

Aside from changes of one sort or another in the

shape of the fluorescence spectra, there also occurs a significant change in their position as the temperature is varied. The changes in the position of the maxima in the fluorescence spectra of 2-acetylanthracene and 3-aminophthalimide as the temperature is varied are represented in Fig. 3. It can be seen from the figure that, in all the solvents investigated, the temperature dependences of the shift in the band maxima for both 2-acetylanthracene and 3-aminophthalimide are expressed by curves with maxima. The gradual shift of the fluorescence maximum toward shorter wavelengths as the temperature is raised above the temperature corresponding to the longest-wavelength position of the spectrum (t_{max}) may be compared with the diminution in the value of the static dielectric constant (curves 3 in Fig. 3, a, b) and apparently has the same cause—the disorienting influence of the thermal motion of the molecules. The diminution of the influence of this factor as the temperature is lowered leads to an increase in the value of ϵ_{stat} down to the temperature at which the solution becomes so viscous that orientation of the dipoles is highly hindered and the quantity ϵ_{stat} begins to fall sharply.

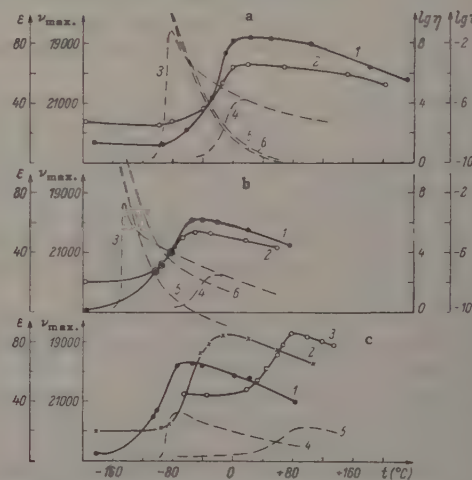


Fig. 3. Temperature dependences of the positions of the maxima of the fluorescence spectra of 2-acetylanthracene and 3-aminophthalimide in solutions, and also of the values of the dielectric constants ϵ , the viscosity η , and the relaxation time τ of the corresponding solvents. a, b—Solvents: glycerol and isobutyl alcohol respectively. Curve 1—position of the spectra of 2-acetylanthracene; curve 2—position of the spectra of 3-aminophthalimide; curve 3—variation of $\epsilon_{\text{stat}} = f(t)$ (according to ref. 10); curve 4—variation of $\epsilon = f(t)$ at a frequency of 6×10^6 cycles (according to ref. 11); curve 5—variation of $\ln \eta = f(t)$ (according to ref. 10); curve 6—variation of $\log \tau = f(t)$ (according to ref. 10). c: Curves 1, 2, 3—positions of the spectra of 2-acetylanthracene in *n*-butyl alcohol, ethylene glycol, and glucose respectively (according to ref. 5); curve 4—variation of $\epsilon = f(t)$ for *n*-butyl alcohol at a frequency of 5×10^5 (according to ref. 12); curve 5—variation of $\epsilon = f(t)$ for glucose at a frequency of 9.2×10^3 cycles (according to ref. 13).

As can be seen from Fig. 3, in the case of glycerol, reaches its maximum value at -80° , and in the case of isobutyl alcohol at -144° . Evidently, if the quantity determined the position of the fluorescence spectra, one should expect in them a maximal shift toward lower frequencies at these same temperatures. Actually, the position of the maxima of the fluorescence bands of solutions of 2-acetylanthracene and 3-aminophthalimide in glycerol at -80° and in isobutyl alcohol at -144° is close to their shortest-wavelength position, which is characteristic for the lowest temperatures studied (-183° and -196°), where the solvent may be considered completely solid. The spectra assume their extreme long-wavelength position at significantly higher temperatures: around 10° in glycerol and around -50° in isobutyl alcohol.

These facts show that, at high solvent viscosities, comparison of the position of the fluorescence spectrum with the value of the static dielectric constant has no significance. If we seek a connection between the position of the fluorescence maximum and the value of the dielectric constant, then, as can be seen from Fig. 3, an agreement with respect to temperature dependence can be found not with the static dielectric constant, but with the dielectric constant measured at high field-reversal frequencies (10^6 - 10^7 cycles), i.e., in the case where the field reversals are so frequent that the dipoles do not succeed in following the field, and at relatively high temperatures where the viscosities are not yet great. Evidently, it is natural to consider that the temperature dependence of the shift in the maximum of the fluorescence spectrum at temperatures less than $t_{\max}$, as well as the temperature dependence of ϵ as measured at high frequencies, is connected with the extent to which the orientation of the solvent molecules, which is realized during the time of existence of the field, approaches the equilibrium orientation for a given field.

It follows from an examination of Fig. 3 that, in the series of solvents investigated, the temperature corresponding to the maximal long-wavelength shift of the spectrum has the greatest value (80°) for a solution in glucose and diminishes progressively on going over to solutions in glycerol (10°), ethylene glycol (-20°), and the butyl alcohols (-50° , -70°); i.e., in the same order as that in which the viscosity of the solvents diminishes. However, this connection is of only a qualitative character, since the absolute viscosity values at $t_{\max}$ for the different solvents differ sharply, being approximately equal to 1.5×10^3 poises for glucose, 40 poises for glycerol, 5 poises for ethylene glycol, and 1 poise for isobutyl alcohol. There is nothing unexpected in this, since the viscosity does not by itself determine the rate of establishment of the equilibrium orientation of the solvent molecules around the excited molecule. For example, it seems entirely natural to suppose that, at the same viscosity, this rate will be greater in the case of glycerol or ethylene glycol than in the case of butyl alcohol, since, in consequence of the greater saturation of the molecules of these solvents by hydroxyl groups, their movements in attaining the equilibrium arrangement must be less.

A considerably better correspondence is observed on

comparison of the values of $t_{\max}$ with the relaxation time of the solvent molecules at the same temperature. The curves for the temperature dependence of the relaxation time are presented in Fig. 3 for glycerol and isobutyl alcohol, as determined from the temperature dependence of ϵ at different frequencies.¹⁰ As follows from the figure, at temperatures corresponding to the longest-wavelength position of the fluorescence maxima of 2-acetylanthracene and 3-aminophthalimide, the relaxation times in glycerol and isobutyl alcohol are near each other and equal to approximately 10^{-8} sec, i.e., a quantity of the order of the duration of the excited state.

Thus the investigation which has been made into the influence of temperature on the position and shape of the fluorescence spectra of solutions of 2-acetylanthracene and 3-aminophthalimide in a series of hydroxyl-containing solvents shows that, in this case, the influence of the solvent on the fluorescing molecule is fundamentally determined not by its macroscopic properties (the quantities ϵ and η), but by a close-order interaction between the excited molecule and the solvent molecules which orient themselves in a particular manner relative to it.

It should be noted that the items investigated in the present work are apparently not to be considered as peculiar to it. Examination of the structure of compounds in which one observes a strong dependence of the position of the spectra on the solvent, and of the solvents which show the strongest influence on the spectra, allows one to suppose that close-order interactions play a decisive role in the majority of cases when there is a strong dependence of the position of the spectrum on the solvent. It is also feasible that they may have important significance in the case of weaker solvent effects on the spectrum as well. In any case, there is no basis for neglecting such a possibility at the present time.

REFERENCES

1. N. G. Bakhshiev, Opt. i Spekr. 7, 52 (1959), Optics and Spectroscopy 7, 29 (1959); Izvest. Akad. Nauk SSSR, Ser. Fiz. 22, 1387 (1958).
2. V. V. Zelinskii and V. P. Kolobkov, Opt. i Spekr. 5, 423 (1958).
3. L. G. Pikulik and M. A. Solomakho, Opt. i Spekr. 8, 338 (1960), Optics and Spectroscopy 8, 180 (1960).
4. A. S. Cherkasov, Doklady Akad. Nauk SSSR 130, 1288 (1960).
5. A. S. Cherkasov, Izvest. Akad. Nauk SSSR, Ser. Fiz. 24, 591 (1960).
6. V. P. Klochkov, Zhur. Fiz. Khim. 29, 1432 (1955).
7. V. P. Klochkov, Opt. i Spekr. 1, 546 (1956).
8. L. G. Pikulik, Opt. i Spekr. 2, 676 (1957).
9. A. S. Cherkasov, Opt. i Spekr. 9, 540 (1960), Optics and Spectroscopy 9, 285 (1960).
10. P. P. Kobeko, E. V. Kuvshinskii, and N. I. Shishkin, Zhur. Tekh. Fiz. 8, 715 (1938).
11. S. Mizushima, Physik. Z. 28, 418 (1927).
12. C. P. Smyth and W. N. Stoops, J. Am. Chem. Soc. 51, 3330 (1929).
13. S. B. Thomas, J. Phys. Chem. 35, 2103 (1931).

ON DAVYDOV SPLITTING AND POLARIZATION RATIO IN THE REGION OF THE FIRST ELECTRONIC TRANSITION OF ANTHRACENE CRYSTAL

M. S. Brodin and S. V. Marisova (pp. 473-476)

Received 6 June 1960

The measured values are given of Davydov splitting $\Delta\nu$ and of the polarization ratio K for three fundamental bands of the first electronic-vibrational transition of the anthracene crystal at $T = 20^\circ\text{K}$. It is pointed out that an inaccuracy of orientation of the light vector incident on the crystal along the b -crystal axis has a strong influence on these quantities, resulting in a decrease in their values. This explains the fact that almost all published values of $\Delta\nu$ and K are much smaller than those obtained in the present work, in which these errors are eliminated.

INTRODUCTION

There are many papers dedicated to the study of the polarized absorption spectrum of anthracene crystals.¹⁻¹⁰ The papers by Craig and Hobbins²⁻⁴ are among the most complete ones. The results of the theory of light absorption by molecular crystals developed in these papers, which is a further development of the theory by Davydov,¹¹ are compared with the experimental data obtained for anthracene in the same above quoted papers. The theory takes into consideration the overlapping of wave functions of the various molecular states in this crystal and predicts certain new effects: a redistribution of intensity among the bands of adjacent electronic transitions, a change of the magnitude of the exciton splitting, etc. The most essential experimental quantities used for testing the theory are the Davydov splitting and the polarization ratio.* However, very careful measurements show that

*The polarization ratio is usually defined as the ratio of areas under the absorption curves related to light polarization along two selected crystallographic axis.

these values were determined erroneously in the majority of papers, including refs. 2 to 4. It seems to us that the error is of a general nature, and is connected with an insufficiently precise orientation of the light vector which is parallel to the selected crystallographic axis; the error may occur when only one polarizer is used. This error results in the appearance of the second wave of the usual double refraction and in its overlapping of the spectrum component under study. We know of only one paper⁹ in which this circumstance is taken into consideration, with the result that the splitting obtained at a temperature of 90°K was several times larger than that obtained in all other papers. However, in that paper the influence of the light overlapping upon the shape of the band under study, and on the polarization ratio was not pointed out. It seems proper to report the experimental results obtained by using a more precise procedure, because improving the accuracy of these values may lead to an essential improvement of the theory.

EXPERIMENTAL DETAILS AND RESULTS OBTAINED

In order to eliminate the error of light overlapping, we used in the experimental setup two parallel polarizers, which were placed in front of and behind the crystal (a Glan-Thomson prism and a spar, respectively). The function of the second polarizer is to provide an additional

filtration of the "false" light from the second wave of the double refraction by the crystal, which is caused by a not precise orientation of the crystal axis along the vibrations in the first polarizer.* Its introduction is es-

*It is not difficult to estimate that with an error α in the orientation of the crystal relative to the polarizer, the introduction of the second polarizer makes the intensity of the overlapping light weaker in proportion to $\sin^2 \alpha$, that is, by about two orders of magnitude.

essential for the study of the long wavelength bands of the strongly absorbing b -component of the spectrum, particularly at low temperatures, when the bands become narrower and the dichroism is more pronounced.*

*The danger of the false light overlapping is increased at low-temperature investigations because of a possible depolarization by the cryostat windows caused by thermal stresses.

It is easy to calculate that without the additional filtration in case of an inaccurate orientation of the polarizer along the b -axis, amounting to an error of 2 to 4° , the intensity of false light of the a -wave at the crystal exit might become comparable with the intensity of the basic wave which is greatly weakened by absorption. Figure 1 demonstrates the influence of the false light in the case of a band of pure electronic transition¹ of the b -component in the anthracene spectrum: curve 2 represents a typical distortion of the contour of this band obtained with one polarizer, and curve 1—the contour corrected by the use of a second polarizer (curve 3 corre-

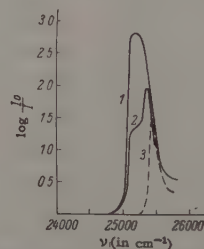


Fig. 1. The influence of the false light on the contour of a pure electronic transition band of the b -component of the spectrum of the anthracene crystal ($T = 20^\circ\text{K}$). Curve 1—contour of the undistorted band; curve 2—typical contour of a band distorted by false light; curve 3—contour of a band of the a -component of the spectrum.

The crystals were grown, as usual, by the sublimation method, and were placed in optical contact with the quartz plates.

For the investigation at low temperatures, the plates, together with the crystals, were placed in a metallic cryostat with quartz windows. The intensity measurements were made by photographic photometry using a spectrograph with a large dispersion DFS-3. The light source was a powerful xenon lamp DKSSH-1000. The intensity reference points were selected in spectral regions close to the band of the longest wavelength, where the crystal does not absorb noticeably. With this selection of reference points, the reflection of light from the crystal is automatically eliminated to a large extent. Although in the immediate vicinity of the band maximum the reflection is somewhat different from that in the reference points (it is greater on the long wavelength side, and smaller on the short wavelength side), its influence upon integration over the whole band is practically eliminated, as a calculation has shown.

The absorption spectra of a number of anthracene crystals of various thicknesses (0.05 to 0.3μ) were obtained; however, we have succeeded in the photometric measurements over the whole band, including the maxima of the strongest bands of the b-components, only with the thinnest crystals ($d \leq 0.1\mu$). For some wavelengths in the vicinity of the maximum of the absorption band of the b-component at $T = 20^\circ\text{K}$, a nonmonotonic (oscillating) dependence of the optical density $\log I_0/I$ on the crystal thickness was found, which was described and explained in the preceding papers.¹² We are not going to discuss this matter any further; however, it is necessary to have in mind that in connection with this, differences are possible in the polarization ratios and in the splittings in the spectra of crystals of various thicknesses.

Figure 2 gives the optical densities curves $\log I_0/I$ in polarized light ($\parallel a$ and $\parallel b$) at $T = 20^\circ\text{K}$ for a crystal of 0.1μ thickness. The positions of the main maxima for a- and b-components of the spectrum, and the values of Davydov splitting for the respective bands obtained from these curves are given in Table 1. The polarization ratios K for the three mentioned bands are also given in this table.

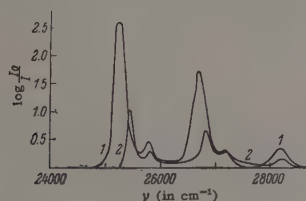


Fig. 2. The optical density curves of an anthracene crystal ($d = 0.1\mu$, $T = 20^\circ\text{K}$). Orientation of the light vector: curve 1— $\parallel b$; curve 2— $\parallel a$.

The values given in Table 1 are in general different for different crystals. This is particularly true with respect to the polarization ratio. For instance, we had crystals for which the value of K in the first and in the second bands was 6, and even higher. However, we have not encountered cases where the value of K for the bands No. 1 was less than 4.

The values of $\Delta\nu$ and of K averaged for several crystals of various thicknesses (0.05 to 0.1μ) are given in Table 2.

Table 1

No. of the band	ν_m (in cm^{-1})		$\Delta\nu$ (in cm^{-1})	K
	$\parallel b$	$\parallel a$		
1	25213	25432	220	5
2	26680	26830	150	3
3	28200	28280	80	3

Table 2

No. of the band	$\Delta\nu$ (in cm^{-1})	K
1	230	5
2	145	4.5
3	80	3.2

DISCUSSION OF RESULTS AND COMPARISON WITH THE PUBLISHED DATA

The following conclusions can be made with respect to the results obtained in the present work:

1. The value of the dichroic splitting $\Delta\nu$ at $T = 20^\circ\text{K}$ for the first band of a pure electronic transition is, on the average, 230 cm^{-1} . As the order of the vibrational bands increases, the splitting decreases systematically and for the band No. 3 is, on the average, 80 cm^{-1} . This tendency toward decreasing $\Delta\nu$ is regular and is connected with an increased effective mass of the exciton for vibrational bands. Actually, it is reasonable to assume that the velocity of the exciton which is perturbed by the oscillation is decreased.

The absolute values of the splittings which we have obtained are, on the average, several times larger than those reported in the literature. For instance, in ref. 4, for the three fundamental bands the following values of $\Delta\nu$ are given: at $T = 20^\circ\text{K}$ —17, 29, and 48 cm^{-1} ; for $T = 290^\circ\text{K}$ —65, 58, and 40 cm^{-1} (the different direction of changes of $\Delta\nu$ from one band to another at two temperatures is peculiar). It follows from some papers, for example, ref. 7, that within the errors of measurements, the positions of a- and b-bands coincide. We believe that this result is connected with the aforementioned light overlapping the bands belonging to the b-component of the spectrum, and by the resulting apparent displacement of their maxima toward the larger frequencies (in the direction of the a-component of the spectrum). One can also understand from the same point of view the different trends of changes of $\Delta\nu$ at 20° and 290°K . As a matter of fact, the influence of false light is especially important at low temperature and is more pronounced in the sharp No. 1 and No. 2 bands.

In one of the quoted papers by Craig and Hobbins³ the values of the Davydov splitting are also given, calculated for the transitions of the B_{3u} and B_{2u} symmetry. In the case of B_{2u} , which is of interest to us, for the three bands considered here, the values obtained in ref. 3 were: $\Delta\nu_1 = 29\text{ cm}^{-1}$, $\Delta\nu_2 = 31\text{ cm}^{-1}$, and $\Delta\nu_3 = 25\text{ cm}^{-1}$ (they are close to the experimental values obtained in the same work). It seems to us that these low values of $\Delta\nu$ are obtained partly because of the use of a low value for the oscillation strength.* Thus the errors of the experiment and of

*The authors of ref. 3 used the value $f = 0.1$. When the error caused by false light is eliminated, and the correct formula for f is used, in which the refracting index enters as a factor, a value for f is obtained which is actually much larger than 0.1.

the calculation, having the same sign, resulted in the lowering of the true values and made them accidentally close.

There is also a theoretical paper¹³ in which the Davydov splitting for anthracene is calculated by considering the anisotropy in the space of the wave vector. The value of 660 cm^{-1} for the splitting of the short wavelength

transition obtained in that paper, in the first approximation of the theory, is much closer to that obtained by us, experimentally, than the values calculated in ref. 3.

2. The polarization ratios obtained by us for three fundamental bands (5, 4.5, and 3.2) are larger than those obtained in refs. 3, 4, 6, and 10. For instance, in ref. 4 a value $K = 3$ is obtained. As has been previously mentioned, we had crystals for which in the first two bands K was approximately 6, and this value is not much lower than the value 7 obtained from the model of an "oriented gas." This means that in the case of the crystals mentioned (in the region where the bands originate) it is hardly possible to consider a substantial effect of the intensity redistribution between two transitions as predicted in ref. 3. As our measurements have shown, in this case there is a much larger effect—the dependence of the transparency on the thickness—that might affect the polarization ratio.

The writers express their gratitude to A. F. Prikhod'ko for a discussion of the results of this work.

REFERENCES

1. I. V. Obreimof and A. F. Prikhod'ko, *Phys. Z. Sowjetunion* **9**, 40 (1936).
2. D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, 539 (1955).
3. D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, 2302 (1955).
4. D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, 2309 (1955).
5. M. S. Brodin and A. F. Prikhod'ko, *Opt. i Spektr.* **2**, 448 (1957).
6. A. Bree and L. E. Lyons, *J. Chem. Soc.*, 2662 (1956); L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, 1551 (1959).
7. J. H. Sidman, *Phys. Rev.* **102**, 96 (1956).
8. J. Ferguson and W. G. Schneider, *J. Chem. Phys.* **28**, 741 (1958).
9. H. C. Wolf, *Z. Naturforsch.* **13a**, 414 (1958).
10. M. S. Brodin and A. F. Prikhod'ko, *Opt. i Spektr.* **7**, 132 (1959), *Optics and Spectroscopy* **7**, 82 (1959).
11. A. S. Davydov, "Teoriya pogloshcheniya sveta v molekulyarnykh kristallakh" (Theory of Light Absorption in Molecular Crystals). *Izd. Akad. Nauk Ukrain. SSR, Kiev*, 1951.
12. M. S. Brodin and S. I. Pekar, *Zhur. Eksptl. i Teoret. Fiz.* **38**, 74 (1960), *Soviet Phys.-JETP* **11**, 55 (1961); *Ibid.* **38**, 1910 (1960), *Soviet Phys.-JETP* **11**, 1373 (1961).
13. D. Fox and S. Yatsiv, *Phys. Rev.* **108**, 938 (1957).

MAGNETIC ROTATION OF THE PLANE OF POLARIZATION OF LIGHT IN THE IMPURITY ABSORPTION REGION

A. F. Lubchenko (pp. 477-486)

Received 21 May 1960

General formulas are obtained for the curves describing the absorption, dispersion, and rotation of the plane of polarization in the region of impurity absorption of light in the presence of a constant external magnetic field; their dependence on temperature and other parameters characteristic of the solvent and its interaction with the impurity centers is established. It is shown that in the case of strong coupling between the electronic excitation of the impurity and the lattice vibrations, the curves of absorption, dispersion, and rotation of the plane of polarization are asymmetric, their asymmetry increasing with decreasing temperature; in the case of weak coupling, the curves of absorption, dispersion, and rotation of the plane of polarization are respectively in the form of sums of curves of the same type as for the classical oscillator.

INTRODUCTION

The theory of the absorption and dispersion of light in the impurity absorption region has been discussed in many papers.¹⁻⁷ Fairly general formulas have been obtained for the absorption and dispersion curves, which agree relatively well with experimental observations. It has been possible to give a qualitative description of the response of these curves to changes in temperature and the nature of the solvent, and to calculate the average radiative lifetime of the impurity center in the excited state. Additional information about the influence of the solvent on the impurity centers can be obtained by studying the rotation of the plane of polarization in the impurity absorption region in the presence of a constant external magnetic field (the Faraday and Makaluzo-Corbino effects). The theoretical study of this problem is taken up in ref. 8, which uses the results of Davidov.⁴ In the present paper, the theory of the magnetic rotation of the plane of

polarization in the impurity absorption region is considered without detailed assumptions about the nature of the impurity center and solvent; the magnetic rotation of the plane of polarization is studied as a function of temperature.

1. THE WAVE FUNCTIONS AND ENERGY LEVELS OF THE SOLUTION

The Hamiltonian of the system (solvent + impurity center) in a constant external magnetic field H directed along the oz axis, can be written in the form*

$$H_0 = H_s + H_{mol.} + W - HM_z,$$

*We are considering a field H such that the Zeeman splitting is greater than the hyperfine structure.

where H_s is the Hamiltonian of the solvent, $H_{mol.}$ is the

hamiltonian of the impurity center, W is the energy operator of the interaction of the impurity center with the solvent, and M_z is the z-component of the total magnetic moment of the solution:

$$M_z = \sum_i \frac{e_i}{2m_i c} [(\mathbf{r}_i \mathbf{p}_i) + 2\sigma_i]_z.$$

For the determination of the stationary states of the solution, we shall assume that we know the solutions of the equation

$$(\mathbf{H}_{\text{mol.}} - H M_z) \varphi_i(rgH) = E_i(H) \varphi_i(rgH),$$

which describes the behavior of the molecule situated in a magnetic field. Then the solution of the equation

$$\mathbf{H}_0 \Psi = E \Psi \quad (1)$$

will be sought in the form

$$\Psi = \varphi_i(rgH) F_i(R). \quad (2)$$

Here r and g are respectively the coordinates of the electrons and the normal coordinates of the impurity molecule, R are the coordinates of the solvent atoms, and l is the complete set of quantum numbers characterizing the states of the optical electrons of the impurity, including the magnetic quantum number m .

After substituting Eq. (2) into Eq. (1), multiplying by $\varphi_i^*(rgH)$, and integrating over the internal variables of the impurity center, we get

$$[E_l + W_{ll} + \mathbf{H}_z] F_l = E F_l,$$

where

$$W_{ll} = \int \varphi_i^*(rgH) W \varphi_i(rgH) dr dg.$$

Since the nuclei of the solvent atoms perform vibrations, in the main, about equilibrium positions which are determined by the condition of minimum potential energy of the solution, then W_{ll} can be expressed in a power series in the displacement from these equilibrium positions. Symbolizing the equilibrium position corresponding to $l = l_0$ (ground state of the system) by R_0 and expanding W_{ll} in a series we obtain, after introducing the normal coordinates,⁹

$$\begin{aligned} \frac{1}{2} \sum_i \hbar \omega_i^l \left(-\frac{\partial^2}{\partial \xi_i^2} + \xi_i^2 + 2 \frac{b_i^l}{\hbar \omega_i^l} \xi_i \right) F(\xi) \\ = (E - W_{ll}(R_0 H) - E_l) F(\xi). \end{aligned} \quad (3)$$

Here

$$\sum_i b_i^l \xi_i = \sum_j \frac{\partial W_{ll}}{\partial R_j} (R_j - R_{j0}),$$

and ω_i^l and ξ_i are the normal frequencies and normal coordinates of the vibrations of the solvent atoms.

Further, letting $\xi_{s1} = -b_s^1/\hbar \omega_s^1$, we rewrite Eq. (3) in the form

$$\frac{1}{2} \sum_i \hbar \omega_i^l \left[-\frac{\partial^2}{\partial \xi_i^2} + (\xi_i - \xi_{s1})^2 \right] F(\xi) = \epsilon F(\xi), \quad (4)$$

where

$$\epsilon = E + \frac{1}{2} \sum_i \hbar \omega_i^l \xi_{s1}^2 - W_{ll}(R_0 H) - E_l.$$

Equation (4) has the well-known solutions

$$\epsilon = \sum_i \hbar \omega_i^l \left(n_i + \frac{1}{2} \right), \quad F(\xi) = \prod_i f_{n_i}(\xi_i - \xi_{s1}),$$

where $f_{n_i}(\xi_i - \xi_{s1}) = c H_{n_i}(\xi_i - \xi_{s1}) \exp[-\frac{1}{2}(\xi_i - \xi_{s1})^2]$; $H_{n_i}(\xi_i - \xi_{s1})$ are the Chebyshev-Hermite polynomials.

In this way, the wave functions of the stationary states of the solution and the energy eigenvalues corresponding to them are written in the form

$$\left. \begin{aligned} \Psi_{l(n_s)} &= \varphi_l(rgH) \prod_i f_{n_i}(\xi_i - \xi_{s1}), \\ E_{l(n_s)} &= E_l(H) + W_{ll}(R_0 H) - \frac{1}{2} \sum_i \hbar \omega_i^l \xi_{s1}^2 + \sum_i \hbar \omega_i^l \left(n_i + \frac{1}{2} \right). \end{aligned} \right\} \quad (5)$$

We now assume that at time $t = 0$ a plane electromagnetic wave

$$\mathbf{E}(\mathbf{r}t) = \frac{1}{2} \mathbf{E}_0 e^{i(\omega t - \mathbf{Q} \cdot \mathbf{r})} + \frac{1}{2} \mathbf{E}_0^* e^{-i(\omega t - \mathbf{Q} \cdot \mathbf{r})} \equiv \mathbf{E}_1 + \mathbf{E}_2.$$

is incident on the system.

Limiting our discussion only to dipole transitions, we can write the energy of the interaction of the impurity center with the electromagnetic field as

$$U = -\sum_i \mathbf{p} \chi \mathbf{E}(0t), \quad (6)$$

where χ , generally speaking, is a tensor quantity that takes into account the difference between the actual field acting on the impurity and the average macroscopic field, and $\mathbf{p}$ is the electric dipole moment operator of the impurity center.

Under the influence of the perturbation (6), the system makes a transition to an excited state, the wave function of which is described by the equation

$$i\hbar \frac{\partial \Phi}{\partial t} = (\mathbf{H}_0 + U) \Phi. \quad (7)$$

The solution of the latter equation will be sought in the form

$$\begin{aligned} \Phi &= \sum_{\substack{l' \in \{l\} \\ (l' \neq l_0)}} b_{l'}(n_s') (t) e^{-\frac{i}{\hbar} E_{l'}(n_s') t} \Psi_{l'}(n_s') \\ &+ \sum_{\substack{l'' \in \{l\} \\ (l'' \neq l_0)}} b_{l''}(n_s'') (t) e^{-\frac{i}{\hbar} E_{l''}(n_s'') t} \Psi_{l''}(n_s''). \end{aligned} \quad (8)$$

Substituting (8) into (7) and using the initial conditions

$$b_l(n_s'') (0) = \delta(l - l_0) \delta(n_s'' - n_s),$$

it is easy to compute the probability amplitude $b_{l'}(n_s')(t)$; after substituting the latter into (8) we obtain the following expression for the wave function of the excited state of the system

$$\begin{aligned} \Phi &= \Psi_{l_0}(n_s) e^{-\frac{i}{\hbar} E_{l_0}(n_s) t} \\ &+ \frac{1}{2\hbar} \sum_{l \in \{l\}} \frac{\prod_s M_{n_s' n_s}^{ll_0} (\chi E_0^* \cdot \mathbf{p}_{l_0}) e^{-\frac{i}{\hbar} [E_{l_0}(n_s) + \hbar \omega] t}}{\Omega_{l_0}^{n_s} + \sum_s \omega_s^l (n_s' - n_s) - \omega - i\Gamma} \Psi_{l'}(n_s'). \end{aligned} \quad (9)$$

Here

$$P_{ll_0} = \langle \varphi_l^* | P | \varphi_{l_0} \rangle, \quad M_{n_s n_s}^{ll_0} = \langle f_{n_s} (\xi_s - \xi_{sl}) f_{n_s} (\xi_s - \xi_{sl_0}) \rangle,$$

$$\begin{aligned} \hbar \Omega_{ll_0}^{n_s} &= E_l - E_{l_0} + W_{ll} - W_{l_0 l_0} \\ &- \frac{\hbar}{2} \sum_s [\omega_s^l \xi_s^2 - \omega_s^{l_0} \xi_{s l_0}^2 - (\omega_s^l - \omega_s^{l_0}) (2n_s + 1)]. \end{aligned}$$

2. CALCULATION OF THE POLARIZATION OF THE SOLUTION

Using the functions (9), it is easy to calculate the polarization P' caused by the impurity centers

$$P' = \sum_j \langle \Phi | P^j | \Phi \rangle - \sum_j \langle \Psi_{l_0(n_s)}^* | P^j | \Psi_{l_0(n_s)} \rangle, \quad (10)$$

where the summation over j signifies the summation over all the impurity centers in unit volume. The total value of the polarization P'' is obtained by averaging Eq. (1) over all initial states*

*Here we have singled out from the complete set of quantum numbers l the magnetic quantum number m .

$$P'' = \sum_{m_0 \{n_s\}} P' \frac{\exp \{-E_{l_0 m_0(n_s)} / kT\}}{Z_1},$$

where

$$Z_1 = \sum_{m_0 \{n_s\}} \exp \left\{ -\frac{E_{l_0 m_0(n_s)}}{kT} \right\}.$$

Thus the polarization caused by transitions in impurity centers is written in the form

$$P'' = P'_1 + P'_1^*,$$

where

$$P'_1 = \frac{1}{\hbar Z_1} \sum_{jlm \{n_s'\}} \frac{\Pi_s |M_{n_s n_s}^{ll_0}|^2 P_{lm, l_0 m_0}^j (P_{l_0 m_0 l m}^j \chi^j E_1)}{\Omega_{ll_0}^{j n_s} + \sum_s \omega_s^l (n_s' - n_s) - \omega + i\Gamma} e^{-\frac{E_{l_0 m_0(n_s)}}{kT}}. \quad (11)$$

The polarization of the solution is caused not only by transitions in the impurity centers, but also by virtual transitions in the solvent molecules; hence the total polarization of the system is written as $P = P'' + P_2 + P_2^*$, where P_2 is the polarization of the solvent. Furthermore, we shall assume that the $l_1 m \{n_s'\}$ states to which these transitions are taking place are from the $l m \{n_s'\}$ states with $l \neq l_1$, so that the virtual transitions to these states introduce a contribution of magnitude $\varepsilon_1(H)$ into the dielectric permeability tensor, ε_1 depending weakly on frequency. Then, expanding $E_{l_0 m_0(n_s)}$ in a series of powers of H :

$$E_{l_0 m_0} = E_{l_0 m_0}(0) + H \zeta_{m_0},$$

and in view of Eq. (11), we shall rewrite the expression $P = P'_1 + P_2$ in the form

$$\begin{aligned} P_1 &= \frac{\varepsilon_1(H) + \varepsilon_2(H) - 1}{4\pi} E_1 \\ &+ \frac{1}{\hbar Z} \sum_{mm'j \{n_s'\}} \frac{\Pi_s |M_{n_s n_s}^{ll_0}|^2 P_{lm, l_0 m_0}^j (P_{l_0 m_0 l m}^j \chi^j E_1)}{\Omega_{ll_0}^{j n_s} + \sum_s \omega_s^l (n_s' - n_s) - \omega + i\Gamma} e^{-H \zeta_{m_0} / kT}. \quad (12) \end{aligned}$$

Here the line over the summation symbol signifies the average over the initial states $\{n_s\}$, and

$$Z = \sum_{m_0} \exp \left\{ -\frac{H \zeta_{m_0}}{kT} \right\}.$$

From Eq. (12) it follows that the calculation of the polarization reduces to a calculation of the expression

$$F_m^j(\omega) - iS_m^j(\omega) = \sum_{\{n_s'\}} \frac{\Pi_s |M_{n_s n_s}^{ll_0}|^2}{\Omega_{ll_0}^{j n_s} + \sum_s \omega_s^l (n_s' - n_s) - \omega + i\Gamma}. \quad (13)$$

The functions $F_m(\omega)$ and $S_m(\omega)$ were calculated to a first approximation in ref. 4 and to a much higher approximation in refs. 5 and 6, on the basis of the properties of the Dirac δ -function. We shall briefly recapitulate this calculation: Starting from the definition of the δ -function

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dx$$

and its property

$$\int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a),$$

the expressions for $F_m^j(\omega)$ and $S_m^j(\omega)$ can be written as

$$\begin{aligned} F_m^j &= \frac{1}{\pi} \int_{-\infty}^{\infty} d\gamma Re \int_0^{\infty} d\mu \frac{(\Omega_{ll_0}^{j n_s} - \omega + \gamma) e^{i\mu\gamma + \theta(\mu)}}{(\Omega_{ll_0}^{j n_s} - \omega + \gamma)^2 + \Gamma^2}, \\ S_m^j &= \frac{\Gamma}{\pi} \int_{-\infty}^{\infty} d\gamma Re \int_0^{\infty} d\mu \frac{e^{i\mu\gamma + \theta(\mu)}}{(\Omega_{ll_0}^{j n_s} - \omega + \gamma)^2 + \Gamma^2}, \end{aligned}$$

where

$$g(\mu) = \frac{1}{2} \sum_s \left[\bar{n}_s e^{i\mu\omega_s^{l_1}} + (\bar{n}_s + 1) e^{-i\mu\omega_s^{l_1}} - (2\bar{n}_s + 1) \right] (\xi_{sl_0} - \xi_{sl_1})^2,$$

$\bar{n}_s = [\exp(\hbar\omega_s/kT) - 1]^{-1}$, and $\bar{\Omega}_{l_1 l_0}^j$ is obtained from $\Omega_{l_1 l_0}^{j n_s}$ by replacing n_s by $\bar{n}_s$.

Further, let $\omega_s^{l_1 m}$ be the maximum value of the frequency $\omega_s^{l_1}$. We choose $\mu = \mu_0$ such that $\mu_0 \omega_s^{l_1 m} = \alpha < 1$. Then if

$$\sum_s \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{sl_0} - \xi_{sl_1})^2 \alpha^2 \left(\frac{\omega_s^{l_1}}{\omega_s^{l_1 m}} \right)^2 \gg 1, \quad (14)$$

it is easily shown that the integral

$$Re \int_{\mu_0}^{\infty} d\mu \exp [i\mu\gamma + g(\mu)]$$

is negligibly small compared to the integral

$$Re \int_0^{\mu_0} d\mu \exp [i\mu\gamma + g(\mu)],$$

and in the latter integral we can express $g(\mu)$ as a power series in $(\mu \omega_s^{l_1})$, confining ourselves to the first terms of the expansion. For the sake of brevity, we set

$$A = \frac{1}{2} \sum_s (\xi_{sl_0} - \xi_{sl_1})^2 \omega_s^{l_1}, \quad C = \frac{1}{2 \cdot 3!} \sum_s (\xi_{sl_0} - \xi_{sl_1})^3 (\omega_s^{l_1})^3,$$

$$B^2 = \sum_s \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{s,10} - \xi_{s,1})^2 (\omega_s^1)^2,$$

$$D = \frac{1}{4!} \sum_s \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{s,10} - \xi_{s,1})^4 (\omega_s^1)^4$$

and using the method of steepest descent to calculate the integrals in $d\mu$, and the theory of residues for the integration over $d\rho$ in the expression for S_m^j , we obtain the following expressions for F_m^j and S_m^j :

$$S_m^j = \frac{\sqrt{\pi}}{2B} \left[1 + \frac{Ca^3}{4B^6} + \frac{Da^4}{8B^8} + \dots \right] e^{-\frac{a^2}{4B^2}}. \quad (15)$$

$$F_m^j = \frac{1}{2B\sqrt{\pi}}$$

$$\times \int_{-\infty}^{\infty} \left[\frac{y + y(y-x)^3 \frac{CT^3}{4B^6} + y(y-x)^4 \frac{DT^4}{8B^8} + \dots}{1+y^2} \right] e^{-\frac{(y-x)^2}{L^2}} dy, \quad (16)$$

where $x = (\bar{\Omega}_{110}^1 + A - \omega)/\Gamma$, $\alpha = \omega - \bar{\Omega}_{110}^1 - A$, and $L = 2B/\Gamma$.

The function S_m^j , as will be seen in what follows, determines the form of the absorption curve; it is easy to see that this curve is asymmetric, and that when T (and consequently, B) increases, the asymmetry of the curve decreases and the curve goes over into a gaussian shape.

The function F_m^j determines the behavior of the dispersion curve. It is easily seen that this curve is also asymmetric relative to a straight line going through the point $x = 0$, perpendicular to the frequency axis. Schematically, F_m^j is drawn in the Figure (curve 4) as a function of frequency (or analogously, curve 5). The asymptotic expressions for F_m^j have the form*:

*The remark of Dexter⁶ regarding the incorrectness of Eq. (42) in ref. 4 cannot be considered as valid; in ref. 4 it was implied that this expression was correct over a region smaller than the half-width of the absorption band; ref. 6 gives an explicit criterion for using this approximation. The use of Eq. 42 in ref. 10 is an unfounded attempt (as the authors realized) to approximate the entire dispersion curve by this equation.

with $|x| < L$,

$$F_m^j = 2 \left[x + \frac{3C}{B^3 L^2} x^3 - \frac{2C}{B^3 L^3} x^4 + \dots \right] \frac{e^{-\frac{x^2}{L^2}}}{L^2 \Gamma};$$

with $|x|/L > 1$, for $x > 0$,

$$F_m^j(x) = \frac{1}{\Gamma} \left[\frac{x}{1+x^2} - \frac{\beta}{2+x^2} \right];$$

for $|x| < 0$,

$$F_m^j(x) = -\frac{1}{\Gamma} \left[\frac{|x|}{1+x^2} + \frac{\beta}{2+x^2} \right],$$

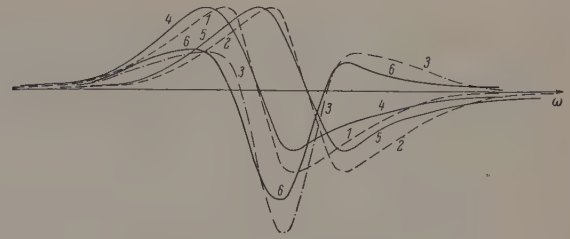
where

$$\beta = \frac{3CL}{2B^3}.$$

When condition (14) is not realized (we shall call this the case of weak coupling between electronic excitation and lattice vibrations), the function $e^{g(\mu)}$ can be represented in the form

$$e^{g(\mu)} = e^{-g(0)} \sum_{\Pi'} J_{\Pi'}(\mu),$$

where



$$J_{\Pi'} = (\gamma! \gamma'!)^{-1} \left(\sum_s b_s e^{i\mu\omega_s^1} \right)^\gamma \left(\sum_s c_s e^{-i\mu\omega_s^1} \right)^{\gamma'},$$

$$g(0) = \sum_s (b_s + c_s), \quad b_s = \frac{\bar{n}_s}{2} (\xi_{s,10} - \xi_{s,1})^2, \quad c_s = \frac{\bar{n}_s + 1}{2} (\xi_{s,10} - \xi_{s,1})^2.$$

Then, if the electronic transition interacts with several types of vibrations $\omega_{s1}^1 = \omega_{s1}^1$, $\omega_{s2}^1 = \omega_{s2}^1$, ..., the functions S_m^j and F_m^j are written in the form⁴:

$$S_m^j = \Gamma e^{-g(0)} \sum_{\gamma_1 \gamma_2 \dots \gamma'_1 \gamma'_2 \dots} \frac{b_1^{\gamma_1} b_2^{\gamma_2} \dots c_1^{\gamma'_1} c_2^{\gamma'_2} \dots}{\gamma_1! \gamma_2! \dots \gamma'_1! \gamma'_2! \dots}$$

$$\times \left[\left[\Omega_{i,10}^j + \sum_s \omega_s^1 (\gamma_s - \gamma'_s) - \omega \right]^2 + \Gamma^2 \right]^{-1},$$

$$F_m^j = e^{-g(0)} \sum_{\gamma_1 \gamma_2 \dots \gamma'_1 \gamma'_2 \dots} \frac{b_1^{\gamma_1} b_2^{\gamma_2} \dots c_1^{\gamma'_1} c_2^{\gamma'_2} \dots}{\gamma_1! \gamma_2! \dots \gamma'_1! \gamma'_2! \dots}$$

$$\times \frac{\Omega_{i,10}^j + \sum_s \omega_s^1 (\gamma_s - \gamma'_s) - \omega}{\left[\Omega_{i,10}^j + \sum_s \omega_s^1 (\gamma_s - \gamma'_s) - \omega \right]^2 + \Gamma^2};$$

the magnitude of Γ in all the preceding expressions can be calculated as in ref. 5.

3. MAGNETIC ROTATION OF THE PLANE OF POLARIZATION

Using Eqs. (12) and (13), we can write the expression for the polarization P_1 in the form

$$P_1 = \frac{e-1}{4\pi} E_1 + \frac{1}{\hbar Z} \sum_{j m m_0} e^{-\frac{\hbar \epsilon_{m_0}}{kT}} P_{i, m, i_0 m_0}^j (P_{i_0 m_0, i, m}^j \chi E) (F_m^j - i S_m^j), \quad (18)$$

where $\epsilon = \epsilon_1(H) + \epsilon_2(H)$. We shall now assume that the matrix elements $P_{11m, 10m_0}$ are different from zero only for $m = m_0 \pm 1$ and $m = m_0$; besides this, if the wave normal is directed along the oz axis, which coincides with the axis of the highest order in solvents of medium and higher syngonies, then the summand with $m = m_0$ in Eq. (18) becomes zero (because $E_{1z} = 0$). Hence, summing over m in Eq. (18), we get

$$P_1 = \frac{e-1}{4\pi} E_1 + \frac{1}{\hbar Z} \sum_{j m_0} e^{-\frac{\hbar \epsilon_{m_0}}{kT}} \{ P_{i, m_0+1, i_0 m_0}^j (P_{i_0 m_0, i, m_0+1}^j \chi^j E_1) (F_{m_0+1}^j - i S_{m_0+1}^j) + P_{i, m_0-1, i_0 m_0}^j (P_{i_0 m_0, i, m_0-1}^j \chi^j E_1) (F_{m_0-1}^j - i S_{m_0-1}^j) \}. \quad (19)$$

Hereafter, the primes on the summation signs indicate summation only over the m_0 for which $m = m_0 \pm 1$ in the excited state.

The matrix elements $P_{1m, 1m_0}$ figuring in Eq. (19) can be written in the form¹¹

$$\begin{aligned} \sqrt{\frac{4\pi}{h}} (l_1 m_0 + 1 | p'_x | l_0 m_0) &= \mp A_{m_0}^{*j}, \\ \sqrt{\frac{4\pi}{h}} (l_0 m_0 | p'_y | l_1 m_0 + 1) &= \mp (i A_{m_0}^{*j}), \\ \sqrt{\frac{4\pi}{h}} (l_1 m_0 - 1 | p'_x | l_0 m_0) &= \pm B_{m_0}^{*j}, \\ \sqrt{\frac{4\pi}{h}} (l_0 m_0 | p'_y | l_1 m_0 - 1) &= \pm (-i B_{m_0}^{*j}). \end{aligned}$$

Substituting these into Eq. (19), we obtain the final expression for the polarization of a solution located in a constant external magnetic field.

In what follows we shall limit ourselves, for the sake of simplicity, to optically isotropic solvents, neglecting the dependence of χ on H . In this case, the components of the induction vector $D_1 = E_1 + 4\pi P_1$ are written

$$\left. \begin{aligned} D_x &= (\epsilon E)_x + RE_x + i\theta E_y, \\ D_y &= (\epsilon E)_y - i\theta E_x + RE_y, \\ D_z &= 0, \end{aligned} \right\} \quad (20)$$

where

$$\begin{aligned} R &= N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} [|A_{m_0}|^2 (F_{m_0+1} - iS_{m_0+1}) \\ &\quad + |B_{m_0}|^2 (F_{m_0-1} - iS_{m_0-1})], \\ \theta &= N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} [|A_{m_0}|^2 (F_{m_0+1} - iS_{m_0+1}) \\ &\quad - |B_{m_0}|^2 (F_{m_0-1} - iS_{m_0-1})], \end{aligned}$$

N being the number of impurity centers in unit volume.

As is known,¹² the dielectric permeability tensor in the presence of a constant external magnetic field satisfies the condition $\epsilon_{ik}(H) = \epsilon_{ik}(-H)$; hence, having set $\epsilon_{ik} = \epsilon'_{ik} + i\epsilon''_{ik}$ and having taken as coordinate axes the principal axes of the tensor ϵ'_{ik} , we can write the tensor ϵ_{ik} in the form

$$\epsilon = \begin{pmatrix} \epsilon' & i\epsilon''_{12} & 0 \\ -i\epsilon''_{12} & \epsilon' & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}.$$

The system (20) is then written in the form

$$\left. \begin{aligned} D_x &= \epsilon' E_x + RE_x + i(\theta + \epsilon''_{12}) E_y, \\ D_y &= \epsilon' E_y + RE_y - i(\theta + \epsilon''_{12}) E_x. \end{aligned} \right\} \quad (21)$$

Equations (21) together with the equation for plane waves in the medium

$$D = N^2 [E - s(\epsilon E)] \quad (22)$$

determine the propagation of light in the solution in the presence of a constant external magnetic field.

The solution of the simultaneous equations (21) and (22) yields

$$\left. \begin{aligned} \frac{D_y}{D_x} &= -i \text{ (left polarization) } N^2_{+} = \epsilon' + R + \theta + \epsilon''_{12}, \\ \frac{D_y}{D_x} &= i \text{ (right polarization) } N^2_{-} = \epsilon' + R - \theta - \epsilon''_{12}. \end{aligned} \right\} \quad (23)$$

Since $N = n - i\kappa$, where n is the refractive index and κ is the absorption coefficient, we find from Eq. (23)

$$\left. \begin{aligned} n^2_{+} - \kappa^2_{+} &= \epsilon' + \epsilon''_{12} + 2N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} |A_{m_0}|^2 F_{m_0+1}, \\ n_{+}\kappa_{+} &= N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} |A_{m_0}|^2 S_{m_0+1}, \\ n^2_{-} - \kappa^2_{-} &= \epsilon' - \epsilon''_{12} + 2N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} |B_{m_0}|^2 F_{m_0-1}, \\ n_{-}\kappa_{-} &= N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} |B_{m_0}|^2 S_{m_0-1}. \end{aligned} \right\} \quad (24)$$

The behavior of $n_{\pm}$ and $\kappa_{\pm}$ in the region of each separate Zeeman component is determined by the expression under the summation sign over m_0 , whereby, since A_{m_0} and B_{m_0} do not depend on ω , the changes in n and κ with frequency are determined by the functions F_m and S_m . Since these functions depend in a complicated way on the intensity of the magnetic field (through Ω_{110}^2), the quantity $n_{-} - n_{+}$, generally speaking, changes with H in a nonlinear manner in the impurity absorption region. Actually, neglecting $\kappa_{\pm}^2$ compared to $n_{\pm}^2$ in Eq. (24), we obtain the following expression for the angle of rotation of the plane of polarization (per unit length):

$$\vartheta = \frac{\pi}{\lambda_0} (n_{-} - n_{+}) \quad (25)$$

$$= \frac{\pi}{\lambda_0 \sqrt{\epsilon'}} \left\{ \epsilon''_{12} + N\chi \sum_{m_0} e^{-\frac{H\epsilon_{m_0}}{kT}} [|B_{m_0}|^2 F_{m_0-1} - |A_{m_0}|^2 F_{m_0+1}] \right\}$$

From this it follows that in the region of impurity absorption, even if we neglect the dependence of Eq. (25) on H through $\exp(-H\epsilon_{m_0}/kT)$, the dependence of ϑ on H will not be strictly linear. We note further that the separation of Eq. (25) into paramagnetic and diamagnetic parts in the classical sense^{13,14} is not possible, since the dependence of ϑ on T is determined not only by the exponential, but also by the functions $F_{m_0 \pm 1}$. In analogy to classical theory¹⁴ of magnetic rotation of the plane of polarization we shall call this expression the "diamagnetic" component of rotation:

$$N\chi \sum_{m_0} [|B_{m_0}|^2 F_{m_0-1} - |A_{m_0}|^2 F_{m_0+1}]. \quad (26)$$

It is easy to see that because of the asymmetry of the functions F_m , the rotation caused by this component will also be asymmetric; however, with increasing temperature the asymmetry caused by Eq. (26) will tend toward zero. With increasing temperature, the role of the "paramagnetic" component of rotation also will decrease proportionately as

$$\frac{H}{kT} \sum_{m_0} \epsilon_{m_0} [|B_{m_0}|^2 F_{m_0-1} - |A_{m_0}|^2 F_{m_0+1}],$$

hence with increasing temperature, the function $d(\omega) =$

$n_- - n_+$ will become symmetric relative to a straight line passing through its minimum and perpendicular to the frequency axis.

Far from the absorption region, when Eqs. (17) are valid, $\varphi(\omega)$ has a form analogous to the classical one. Actually, setting

$$B_{m_0} = B_{m_0}^0 + HB'_{m_0}, \quad Z = Z_0 + HZ_1,$$

$$A_{m_0} = A_{m_0}^0 + HA'_{m_0}, \quad \exp\left\{-\frac{H\zeta_{m_0}}{kT}\right\} \approx 1 - \frac{H\zeta_{m_0}}{kT},$$

$$x_{m_0 \pm 1} = x \pm H\zeta_{m_0 \pm 1},$$

we can write $\varphi(\omega)$ in the form:

for $x > 0$,

$$\varphi = \frac{\pi}{\lambda_0 \sqrt{\varepsilon}} \left\{ \varepsilon_{21} + N\chi H \sum_{m_0} \left[\frac{b_1 \zeta_{m_0-1} + a_1 \zeta_{m_0+1}}{\Gamma x^2} - 2 \frac{b_1 \beta_1 \zeta_{m_0-1} + a_1 \beta_2 \zeta_{m_0+1}}{\Gamma x^3} + \frac{b_2 - a_2}{x} - \frac{b_2 \beta_2 - a_2 \beta_2}{x^2} - \frac{\zeta_{m_0}}{kT} \left(\frac{b_1 - a_1}{x} - \frac{\beta_1 b_1 - \beta_2 a_1}{x^2} \right) \right] \right\};$$

for $x < 0$,

$$\varphi = \frac{\pi}{\lambda_0 \sqrt{\varepsilon}} \left\{ \varepsilon_{21} + N\chi H \sum_{m_0} \left[\frac{b_1 \zeta_{m_0-1} + a_1 \zeta_{m_0+1}}{\Gamma x^2} + 2 \frac{b_1 \beta_1 \zeta_{m_0-1} + a_1 \beta_2 \zeta_{m_0+1}}{\Gamma |x|^3} - \frac{b_2 - a_2}{|x|} - \frac{b_2 \beta_2 - a_2 \beta_2}{x^2} + \frac{\zeta_{m_0}}{kT} \left(\frac{b_1 - a_1}{|x|} + \frac{\beta_1 b_1 - \beta_2 a_2}{x^2} \right) \right] \right\},$$

where

$$b_1 = \frac{|B_{m_0}^0|^2}{\Gamma Z_0}, \quad a_1 = \frac{|A_{m_0}^0|^2}{\Gamma Z_0}, \quad x = \frac{(\bar{Q}_{H_1} I_0 + A - \omega)}{\Gamma},$$

$$b_2 = \frac{(B_{m_0}^0 A_{m_0}^{*'} + B_{m_0}^{*0} B_{m_0}')}{\Gamma Z_0}, \quad a_2 = \frac{(A_{m_0}^0 A_{m_0}^{*'} + A_{m_0}^{*0} A_{m_0}')}{\Gamma Z_0}.$$

The behavior of the function $d(\omega)$ is shown schematically in the Figure (curve 6) for the case in which curves n_- (curve 4) and n_+ (curve 5) have the same amplitude (the case of strong coupling of electronic excitation with lattice vibrations and singlet levels); the

*For singlet levels of atomic impurities a_2 and b_2 equal zero.

Figure also shows the shape of n_+ and n_- for oscillators (curves 1 and 2), and their difference (curve 3).

In the case of weak coupling between the electronic

excitation and lattice vibrations, the behavior of the curve $n_- - n_+$ within each band with $\gamma_1 - \gamma_1' = \text{const.}$ is analogous to the classical case, i.e., to curve 3.

If the amplitudes of n_- and n_+ differ, the behavior of the curve $n_- - n_+$ will depend on the ratio of the amplitudes; however in this case also, for strong coupling between electronic excitation and lattice vibrations, the symmetry of the curve will increase as the temperature increases.

In conclusion, I wish to thank A. S. Davidov for discussions and for his interest in the work.

REFERENCES

1. Huang Kun and A. Rhys, Proc. Roy. Soc. (London) **204**, 406 (1950).
2. M. Lax, J. Chem. Phys. **20**, 1752 (1952).
3. S. I. Pekar, Zhur. Eksptl. i Teoret. Fiz. **22**, 641 (1952).
4. A. S. Davidov, Zhur. Eksptl. i Teoret. Fiz. **24**, 197 (1953).
5. A. F. Lubchenko, Ukrain. Fiz. Zhur. **1**, 120, 265, 281 (1956); Doklady Akad. Nauk Ukrain. SSR, No. 3, 253 (1956).
6. A. F. Lubchenko, Mater. X Vses. soveshch. po spektr. (Proc. Tenth All-Union, Conf. on Spectroscopy) **1**, 289 (1957).
7. R. Kubo and Y. Toyozawa, Prog. Teoret. Phys. (Kyoto) **13**, 160 (1955).
8. O. L. Dexter, Phys. Rev. **111**, 119 (1958).
9. F. Seitz, "The Modern Theory of Solids." McGraw-Hill, New York, 1940.
10. I. S. Gorban' and A. A. Shishlovskii, Doklady Akad. Nauk SSSR **108**, 53 (1957), Soviet Phys.-Doklady **1**, 249 (1957).
11. E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra." Cambridge Univ. Press, 1935.
12. L. D. Landau and E. M. Lifshitz, "The Electrodynamics of Continuous Media." Addison-Wesley, Reading, Mass., 1960.
13. M. V. Vol'kenshtein, "Molekulyarnaya optika" (Molecular Optics). Gosudarst. Izd. Tekh.-Teoret. Lit., Moscow, 1951.
14. W. Schutz, Handbuch d. Exper. Physik **16**, T. 1, Leipzig, 1936.

CALCULATION OF THE OPTICAL PROPERTIES OF SMALL-RADIUS ELECTRONIC CENTERS IN IONIC CRYSTALS

I. V. Abarenkov, N. N. Kristofel' and M. I. Petrashen' (pp. 487-492)

Received 24 May 1960

The paper presents briefly a method of computing the centers of small-radii impurities in ionic crystals. As a result of the successive application of the adiabatic approximation, single-ion approximation, point-lattice approximation, and the single-electron approximation, one succeeds in obtaining formulas applicable for the computation of the center of luminescence in a KCl-Tl crystal, and also of the F-center and U-center in a NaCl crystal.

1. We will investigate the electronic centers in alkali halide crystals, the effective electronic radius of which is not large (of the order of 2-3 of the lattice constants). For example, the impurities center of luminescence (impurity of the activator on a lattice site) and defective centers of the F-center and U-center types, belong to such centers. With some reservations one can also consider as such centers the individual ions of the base of the crystal. Optical properties of such centers are determined by the fact that the absorption and radiation of light in them corresponds to electronic-vibration transitions. Their spectrum has a substantially vibrational character; it is therefore customary to say (regrettably, from our point of view), that the center of radiation interacts with the vibrations of the crystal.

In the theoretical consideration of the absorption spectrum $K(\nu)/\nu$ and of the radiation spectrum $J(\nu)/\nu^3$ of the electronic centers, it is convenient to compute these, making use of the concept of moments of the spectrum. The form of these spectra is close to a Gaussian; therefore one may limit the computations to that of the moments M_0 , M_1 , and M_2 of the zero, first, and second orders. Then the basic characteristics of the spectrum, the frequency $\nu_{\max}$, corresponding to the maximum of the band, and the half-width H of the band is expressed in terms of the moments as follows:

$$\left. \begin{aligned} \nu_{\max} &= \frac{M_1}{M_0} \\ H^2 &= 8 \ln 2 \left[\frac{M_2}{M_0} - \left(\frac{M_1}{M_0} \right)^2 \right] \end{aligned} \right\} \quad (1)$$

To compute the moments M_0 , M_1 , and M_2 one must know the adiabatic potentials of those states of the center for which the transitions are being considered, i.e., the expressions for the energy of the center $W(R)$ as a function of the configuration of the nuclei of the crystal. Then in the harmonic approximation, the moments are determined by the formulas

$$\left. \begin{aligned} \frac{M_1}{M_0} &= \nu_0 - \frac{1}{2} \sum_i \frac{\omega_i^2 - \delta_{ii}}{4\pi\omega_i} \operatorname{cth} \beta_i \\ \frac{M_2}{M_0} &= \left(\frac{M_1}{M_0} \right)^2 + \frac{1}{2} \sum_i \frac{\hbar}{\omega_i} \left(\frac{\delta_{ii}}{\hbar} \right)^2 \operatorname{cth} \beta_i \\ &+ \frac{1}{2} \sum_i \left(\frac{\omega_i^2 - \delta_{ii}}{4\pi\omega_i} \right)^2 \operatorname{cth}^2 \beta_i + \frac{1}{2} \sum_{i,k} \frac{(\delta_{ik})^2}{4\pi\omega_i 4\pi\omega_k} \operatorname{cth} \beta_i \operatorname{cth} \beta_k \end{aligned} \right\} \quad (2)$$

where ν_0 is the frequency of the optimum transition corresponding to the distance between potential levels of the initial and final states at the equilibrium point of the initial state, ω_i is the frequency of the i -th normal mode

of the initial state (one must consider all normal modes of vibration accounting for the optical and acoustical branches), δ_i and δ_{ik} are the first and second derivatives of the adiabatic potential of the final state in terms of the normal coordinates of the initial state, and $\beta_i = \hbar\omega_i/2kT$.

When one considers impurity or defective centers one must take into consideration that while they are present in the crystal there appear local oscillations, the amplitude of which is rapidly attenuating with distance from the defect. For centers having small radii the local oscillations are apparently playing a basic role. Experiment indicates that for such centers the half-widths of the absorption and radiation spectra differ considerably from each other, and consequently, the oscillation frequencies of the center in the ground and the excited states are different; this can take place only for local oscillations.

Therefore, in deriving the expression for the adiabatic potential, we are limiting ourselves to a consideration of the displacement of the ions closest to the center under study. At the same time we are singling out in the crystal a certain quasi molecule, the dimensions of which are determined by the number of the ions, the displacements of which are being considered. Adiabatic potential, by definition, is the eigenvalue in the equation for the wave function $\Phi(x, R)$ of the electronic state of the crystal; x is the set of the spin and space coordinates of the electrons, and R determines the spacial configuration of the nuclei. This equation has the form

$$H(r, R) \Phi(x, R) = W(R) \Phi(x, R), \quad (3)$$

where $H(r, R)$ is the operator of the energy of the electronic state of the crystal. Apparently, one can determine $\Phi(x, R)$ only approximately and it is necessary to compute the adiabatic potential $W(R)$ independent of the determination of Φ . Therefore the accuracy of the computation of $W(R)$ can be considerably higher than that of Φ . In applying the perturbation theory to the model used for the approximate determination of Φ , we may in the expression for W account for effects which were wholly disregarded or only partly accounted for in the computation method of Φ .

2. The electronic centers which we consider in the ionic crystals represent nearly closed subsystems. Therefore the operator $H(r, R)$ can be conveniently expressed in the form

$$H(r, R) = \sum_p H_p + \frac{1}{2} \sum_{p,q} U_{pq}, \quad (4)$$

where

$$H_p = - \sum_k^{(p)} \frac{1}{2} \Delta_k - \sum_k^{(p)} \frac{Z_p}{|r_k - R_p|} + \frac{1}{2} \sum_{j,k}^{(p)} \frac{1}{r_{jk}}$$

is the operator of the energy of the free ion, and

$$U_{pq} = - \sum_k^{(p)} \frac{Z_q}{|r_k - R_q|} - \sum_k^{(q)} \frac{Z_p}{|r_k - R_p|} + \sum_i^{(p)} \sum_k^{(q)} \frac{1}{r_{ik}} + \frac{Z_p Z_q}{R_{pq}}$$

is the operator of the energy of the interaction of the ions p and q ; $\sum^{(p)}$ represents the summation with re-

spect to the electrons of the ion p . We will approximately represent the wave function $\Phi(x, R)$ of the electronic state in the form of a symmetrical linear combination of the products of the wave functions $\Phi_p(x_1, \dots, x_{n_p}, R)$ of separate ions; the symmetry of Φ_p is determined by the ion p alone. Thus for the function Φ_p one can write

$$\left\{ H_p - \sum_{n=1}^{n_p} V_p(r_n) + Z_p V_p(R_p) \right\} \Phi_p + \mathcal{A}_p \Phi_p = W_p(R) \Phi_p \quad (5)$$

$p = 1, 2, \dots, N,$

where

$$V_p(r) = \sum_{q=1}^N \left[\frac{Z_q}{|r - R_q|} - \int \frac{\rho_q(r', R)}{|r - r'|} d\tau' \right]$$

is the potential of the electrostatic field generated by all the ions except ion p ; $\rho_q(r', R)$ is the electronic density of ion q ; $\mathcal{A}_p$ is the operator corresponding to the exchange operator in the method of Hartree-Fock.

If the crystal contains an impurity or defective center, then one of the equations of the system corresponds to this center.

A self-consistent solution of this system does not appear to be a realistic problem, but its every individual equation may be considered as a Schrödinger equation for a separate quantum-mechanical subsystem (of the central ion) which is located in the effective field of the crystal.

Apparently, as a central ion we may take in succession all the ions of the base and the ions of the impurity.

In place of the effective field, where the central ion is located, in the first approximation we substitute the field of a rigid point lattice with the potential

$$V_p^{(0)}(r) = \sum_{q=1}^N \frac{I_q}{|r - R_q^{(0)}|} \quad (6)$$

Computations indicated that in this approximation one can succeed in obtaining the wave functions, thus making it possible to determine fairly accurately the basic characteristics of the central ion.^{1,2} Accounting for the extended (nonpoint) ions closest to the central ion permits one to improve the accuracy of these characteristics.

We are considering the wave function of the central ion in a single-electron approximation. Since the field of the crystal has a weak influence upon the internal electronic shells of the central ion, we are taking the corresponding functions of a free ion as the wave functions of the electrons of these shells. For the wave functions of the optical electron of the central ion we get the equation

$$(H_{pk} + V_p^{(0)}(r)) \varphi_k(r) = \lambda_k \varphi_k(r), \quad (7)$$

where the field of the inner shell of the central ion is also replaced by an effective field, which assures that the function $\varphi_k(r)$ is orthogonal to the wave functions of the internal electrons.

In considering the problem further it is necessary to take into account the symmetry of the system: let us consider that the crystal has cubic symmetry. In Eq. (7) one cannot separate the variables. Therefore let us express $V(r)$ in the form of a series of cubic harmonics of an identical representation,³ and the function $\varphi_k(r)$ we represent in a series of cubic harmonics of the form of Γ_i , corresponding to the state of the electron considered, i.e., in the form

$$\varphi_k(r) = \sum_y \frac{1}{r} f_y(r) K_y^{T_i}(\theta, \varphi). \quad (8)$$

Substituting these expansions into (7), we obtain an infinite system of integral-differential equations for the function of $f_y(r)$. The exact solution of this system is also impossible, but since the central ion represents an almost closed subsystem, then in the expansion of (8) the terms after the first are playing the role of a correction and one can find the approximate solution of (7) in one of the following three ways.

(a) In each of the equations of the system for $f_y(r)$ let us drop the terms playing the role of corrections with respect to the function which is being determined in this equation. Then every following equation of the system contains one function more than the preceding, and the equations may be solved in succession, starting with the first. The parameter λ , entering all equations, is determined in advance by the method of the perturbation theory in the application to Eq. (7).

(b) We are considering the variational problem, corresponding to Eq. (7), of the functional

$$J = \int \varphi_k(r) [H_{pq} + V_p^{(0)}(r) - \lambda] \varphi_k(r) d\tau.$$

Taking comparison functions in the form of segments of the series (8) and performing the integration with respect to angles, from the condition that $\delta J = 0$, we obtain one equation for the radial coefficient of the first comparison function, a system of two equations for two radial coefficients in the second comparison function, and so on. The application of the method of solution of these equations and the approximations obtained in this manner, to the solution of Eq. (7), is investigated in ref. 2.

(c) We replace the potential of the field of the point lattice in Eq. (7) in its turn by a potential of some effective field and we construct a radially symmetrical approximate solution of Eq. (7). At the same time the eigenvalue λ is also preliminarily determined. This method is described in detail in ref. 4.

3. Let us proceed with the determination of the adiabatic potential, i.e., of the eigenvalue in Eq. (3) for the wave function Φ of the electronic motion. This function in the single-ion approximation and in the approximation of the point lattice will be the eigenvalue of the equation

$$\left[\sum_p H_p - \sum_p \sum_k^{(p)} V_p^{(0)}(r_k) \right] \Phi^{(0)} = \Lambda \Phi^{(0)}. \quad (9)$$

It is convenient to determine the adiabatic potential by applying the perturbation theory method with respect to Eq. (3) and by considering Eq. (9) as nonperturbed. Then in the second approximation of the perturbation theory we will have

$$W = W_1 + W_2 = \int \Phi^{(0)} H(r, R) \Phi^{(0)} d\tau + \sum_i \frac{\left| \int \Phi^{(0)} H'' \Phi_i^{(0)} d\tau \right|^2}{\Lambda - \Lambda_i}, \quad (10)$$

where the perturbation operator is

$$H'' = \frac{1}{2} \sum_{p,q} U_{pq} + \sum_p \sum_k^{(p)} V_p^{(0)}(r_k),$$

$\Phi^{(0)}$ is the eigenfunction of (9), corresponding to the state under investigation, and $\Phi_i^{(0)}$ and Λ_i designate the remainder of the eigenfunctions and eigenvalues of Eq. (9).

Let us look separately at the terms W_1 and W_2 in expression (10). To compute W_1 we make use of the fact that in a single-electronic approximation the function $\Phi^{(0)}$ is expressed in terms of the function $\varphi_k(\mathbf{r})$ of the central ion; the methods of construction of these are given in the preceding paragraph. We will have

$$\Phi^{(0)} = \det \{\psi_i(x_k)\},$$

where

$$\psi_i(x) = \sum_k \left\{ (1 + S)^{-\frac{1}{2}} \right\}_{ki} \varphi_k(x)$$

are orthonormalized linear combinations of the function $\varphi_k(x)$. The elements of matrix S will be⁵:

$$S_{ik} = \int \varphi_i(x) \varphi_k(x) dx - \delta_{ik}.$$

In this approximation

$$W_1 = \frac{1}{2} \sum_{p,q} \frac{Z_p Z_q}{R_{pq}} + \sum_k (k|k|k) + \frac{1}{2} \sum_{i,k} \{ (ki|u|ki) - (ki|u|ik) \},$$

where

$$h = -\frac{1}{2} \Delta - \sum_p \frac{Z_p}{|\mathbf{r} - \mathbf{R}_p|} \text{ and } u = \frac{1}{|\mathbf{r} - \mathbf{r}'|}.$$

Separating in this expression the terms related to each individual ion and to the interaction of the ions, we may represent it in the form

$$W_1 = \sum_p E_p + \frac{1}{2} \sum_{p,q} \frac{e_p e_q}{R_{pq}} + \frac{1}{2} \sum_{p,q} W_{pq}(R_{pq}). \quad (11)$$

Here E_p is a value which is independent of the configuration of the nuclei, having also the same form as the energy of the free ion p ; one may consider the value W_{pq} as the energy of the repelling forces of ions p and q . Let us note that in W_{pq} there enters the so-called electrostatic correction, the exchange energy, and S —the energy and the interaction energy of the nuclei.

An independent computation of the second term of (10), containing wave functions other than those of the state under consideration, is also practically impossible. In addition it does not make sense to accurately compute W_2 , a second-order correction, because W_1 is already computed in the single-electron approximation, i.e., by neglecting various correlation effects. One can compute W_2 approximately by two methods. One can, in the first place, break up W_2 into a series in terms of r/R , assuming that r , the distance of the electron to its nucleus, is less than the distance R between nuclei of two adjacent ions and we may limit this breakup to the first term differing from zero. This method, corresponding to the calculation of the so-called van der Waals' forces, was employed in the computation of the center of the luminescence in the crystal KCl-Tl. For the computation of W_2 one can also employ some representations of models; for example, one can consider "point polarizing ions."⁶ This was done in the computation of the F-center and the U-center.

In this manner we obtain an expression for the adia-

batic potential, which can be used to perform computations.

Let us apply this expression to determine the equilibrium positions of the ions in a crystal with an impurity or defective center. We will designate the displacement vectors of the ions from their equilibrium position in an ideal crystal by

$$\mathbf{q}_p = \mathbf{R}_p - \mathbf{R}_p^{(0)}.$$

As already indicated, in the problem under consideration one must account for the displacements of the equilibrium positions of only the ions closest to the center. One can determine the new positions of the equilibrium centers in two ways. In the first place, by utilizing the symmetry of the center of the rotation as a whole, one can express all the components of the vectors $\mathbf{q}_p$ in terms of several (generally one or two) independent components. Then, representing the adiabatic potential as a specified tabulated function of these independent components, one can find its minimum directly.

In the second place, instead of $\mathbf{q}_p$, one can introduce into consideration the symmetric coordinates y_μ . Taking further into account that the displacements from the center, as a rule, are small, we represent W in the form of a segment of a power series of y_μ , limiting ourselves to the square terms (which correspond to the harmonic approximation). Knowing the coefficients of this expression, we can also find the new positions of equilibrium and the normal coordinates. The expression for W will contain the linear term with respect to y_μ , the equilibrium values of which differ from zero. At a nondegenerate state of the central ion, the linear term with respect to y_μ may contain only a totally symmetrical coordinate. For degenerate (perturbed) states the linear term will also contain some non-totally symmetrical coordinates, for which one can find expressions with the help of group theory; the corresponding non-totally symmetrical displacements of the equilibrium positions of the ions, which are superimposed upon the totally symmetrical, lead to a reduction of the symmetry and to the elimination of the degeneracy. This represents the analog of the Jahn-Teller effect for polyatomic molecules.⁷

Having determined the equilibrium positions of the ions by whatever method, we will be able to compute the products of the adiabatic potentials, making use of the same expression of W , and by the formulas (1) and (2) we will be able to find the spectrum characteristics of the center of radiation.

4. The method outlined above allowed us to arrive at a whole series of conclusions, both qualitative and quantitative, about the spectra of the impurity centers in alkali halide crystals.

Basic spectral characteristics of the center of the luminescence were computed in the crystal KCl-Tl,⁸ F-center,^{2,6} and the U-center in the crystal NaCl.⁹ In the computation of the F-center and U-center one more simplifying assumption was made, namely, it was assumed that the center interacts with the ions of the basic substance as with point charges. The computed values of the spectral characteristics are given in the Table.

On the basis of a qualitative analysis of the magnitude of W_1 we obtained some legitimate correlations in the spectra of homologous series of the bases and activators.¹⁰ The effect of uniform compression upon the absorption and radiation spectra of the luminescence of the crystal KCl-Tl was also investigated.¹¹

	KCl-Tl (298° K)		NaCl (0° K)			
	$^1S_0 \rightarrow ^3P_1$		F-Center		U-Center	
	Computed	Experimental	Computed	Experimental	Computed	Experimental
λ_{max} of the absorption	4.64	5.02	2.3	2.7	7.00	6.67
λ_{max} of the radiation	3.73	4.06	1.0	1.1	4.47	—
λ_{max} of the absorption	0.25	0.23	0.2	0.3	0.49 (77° K)	0.52 (77° K)
λ_{max} of the radiation	0.50	0.51	—	—	—	—

Note: All values are given in electron volts.

In addition, accounting for the effect of incompletely symmetrical oscillations indicated that the polarization of the radiation must vanish at temperatures higher than 70°K for the center of luminescence in the crystal KCl-Tl, and $\sim 20^\circ\text{K}$ for the F-center in the crystal NaCl.

One must note that the accuracy of the obtained numerical results, in general, is lower than the accuracy of the method. In those cases when the computations must be performed by the method of successive approximations, we usually limit ourselves to the first approximations, after clearing up the character of the convergence. Therefore the agreement with the experimental data could probably be improved.

It is very likely that a quantum-mechanical consideration of the local centers as quasi-molecules in the field of the crystal may prove to be useful also in some other problems.

REFERENCES

1. M. I. Petrashen', G. L. Guman, and M. Balarin, Vestnik Leningrad. Gosudarst. Univ. No. 22, 4, 28 (1958).
2. I. V. Abarenkov, Vestnik Leningrad. Gosudarst. Univ. No. 22, 4, 14 (1958).
3. I. V. Abarenkov, Vestnik Leningrad. Gosudarst. Univ. No. 16, 5 (1958).
4. M. I. Petrashen', I. V. Abarenkov, and N. N. Kristofel', Vestnik Leningrad. Gosudarst. Univ. No. 16, 3, 7 (1960).
5. P. O. Löwdin, Thesis, Uppsala, 1948.
6. I. V. Abarenkov, Opt. i Spekt. 9, 418 (1960), Optics and Spectroscopy 9, 218 (1960); Candidate's dissertation, Leningrad State University, 1959.
7. N. N. Kristofel', Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR, No. 12 (1960).
8. N. N. Kristofel', Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR 10, 3 (1959); Kand. diss., Tartu, 1959.
9. I. V. Abarenkov and I. Kiselev, Opt. i Spekt. 9, 765 (1960), Optics and Spectroscopy 9, 402 (1960).
10. M. Balarin, Ann phys. 6, 120 (1960).
11. N. N. Kristofel', Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR, 10, 43 (1959).

ON THE THEORY OF THERMAL IONIZATION OF F'-CENTERS

A. G. Cheban (pp. 493-499)

Received 10 June 1960

The thermal ionization of F'-centers in ionic crystals is analyzed by taking the polaron effect into account. An expression is derived for the probability of thermal ionization, and a numerical calculation is carried out for NaCl and KCl crystals at room temperature. The value of the effective capture cross section of a polaron by an F-center is also calculated.

INTRODUCTION

Nonradiative transitions of electrons trapped on impurity centers of ionic crystals have been studied in a number of papers. Without attempting to make a complete analysis of these papers, we will point out the following mechanisms causing nonradiative transitions: (1) The nonadiabaticity operator is considered as a perturbation of the principal papers in which this mechanism is studied are refs. 1-4; (2) the potential interaction energy of an electron with acoustical vibrations is considered as a perturbation. As was shown in ref. 5, the transition probability in a discrete spectrum, calculated on the basis of this latter assumption, is 2 to 3 orders of magnitude greater than the probability of a transition generated by optical nonadiabaticity. The probability of the thermal ionization of an F-center was studied in ref. 6, taking the polaron effect into account.

Charge carriers appear in ionic crystals as polarons, not as free (band) electrons, when there is a strong interaction of electrons with lattice vibrations. The polaron effect must therefore be taken into account when quantum transitions in impurity centers are considered. This problem was analyzed for F-centers by Perlin,^{6,7} who introduced polaron variables in the description of bound states.

In our paper⁸ devoted to the photoionization of an F'-center, the following approximation formulas were obtained for the wave functions and the energy of the ground state of the F'-center in polaron variables:

$$\Psi_{s, \dots, n_x, \dots} = \psi_{F'}(r_s) \psi_{F'}(r_x) \varphi_s(\xi) \prod_x \Phi_{x_0}(q'_x - r_x), \quad (1.1)$$

where

$$r_x = q_{x_{F'}} - q_{x_0}, \quad (1.2)$$

Φ_{n_x} are the wave functions of the harmonic oscillators of the crystal lattice; $q_{x_{F'}}$ is the equilibrium position of the lattice coordinate, in which position both electrons are trapped in the ground state of the F'-center; q_{x_0} is the corresponding value for the polaron;^{6,7} $\psi_{F'}(r)$ is the wave-function of the electron trapped in the F' center:

$$\varphi_s(\xi) = \frac{\lambda^{1/2}}{\sqrt{\pi}} e^{-\lambda \xi^2}. \quad (1.3)$$

The energy of the F'-center in the ground state⁹ is equal to

$$H_0 = I_{F'} + \hbar\omega \sum_x \left(n_x + \frac{1}{2} \right) + \frac{3}{2} \hbar\omega, \quad (1.4)$$

Where $I_{F'}$ is the minimum value of the adiabatic potential of the F'-center. The second term in Eq. (1.4)

represents the energy of free longitudinal optical lattice vibrations. The appearance of the last term results from the introduction of the polaron variable ξ .⁶

Taking the polaron effect in account, we will now consider the thermal ionization of an F'-center caused by the interaction of an electron with acoustical vibrations.

2. PROBABILITY OF MULTIPHONON THERMAL IONIZATION OF AN F'-CENTER

Let us examine multiphonon transitions caused by the interaction of the electron with acoustical vibrations. As an operator for this interaction, we will select the Bethe-Sommerfeld potential,¹⁰ which can be expressed for the F'-center as:

$$\hat{W} = -[(\mathbf{u}_1 \nabla \mathbf{w}(r_1)) + (\mathbf{u}_2 \nabla \mathbf{w}(r_2))], \quad (2.1)$$

in which the displacements $\mathbf{u}_1$ and $\mathbf{u}_2$ can be expanded in planar waves

$$\mathbf{u} = \sqrt{\frac{Q_0}{L^3}} \sum_{\mathbf{q}, j} \mathbf{l}_{\mathbf{q}j} (a_{\mathbf{q}j} e^{i\mathbf{q}\mathbf{r}} + a_{\mathbf{q}j}^* e^{-i\mathbf{q}\mathbf{r}}). \quad (2.2)$$

Here Q_0 is the volume of the unit cell; $\mathbf{W}(\mathbf{r})$ is the periodic potential in the frozen lattice; $a_{\mathbf{q}j}$ and $a_{\mathbf{q}j}^*$ are operators for the disappearance and the creation of acoustical phonons; $\mathbf{q}$ is the wave vector of the acoustical wave and $\mathbf{l}_{\mathbf{q}j}$ the unit vector which determines the polarization. Formula (2.2) was obtained under the assumption that the principal role in the interaction with electrons was played by long acoustical waves. The latter assumption is always fulfilled within the confines of polaron theory.¹¹ The wave function of the system in zero approximation (for the ground state) has the form

$$\begin{aligned} & \Psi_{\mathbf{s}, \dots, \mathbf{n}_2, \dots, N_{\mathbf{q}j}} \\ &= \Psi_{\mathbf{F}'}(r_1) \Psi_{\mathbf{F}'}(r_2) \varphi_{\mathbf{s}}(\xi) \prod_{\mathbf{x}} \Phi_{\mathbf{n}_x}(q'_x - r_x) \eta(\dots N_{\mathbf{q}j} \dots). \end{aligned} \quad (2.3)$$

Due to the presence of rapidly oscillating functions, the detail functions $\Psi_{\mathbf{F}'}(r_1)$ and $\Psi_{\mathbf{F}'}(r_2)$ of the F' center appear in (2.3) instead of electron functions "smoothed" out by the method of effective mass. [$\eta(\dots N_{\mathbf{q}j} \dots)$ is the amplitude of the states of the acoustical vibration field.] The energy of the crystal with an F' center can be represented in the form

$$\begin{aligned} & E_{\mathbf{s}, \dots, \mathbf{n}_2, \dots, N_{\mathbf{q}j}} \\ &= I_{\mathbf{F}'} + \hbar\omega \sum_{\mathbf{x}} \left(n_{\mathbf{x}} + \frac{1}{2}\right) + \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j} \left(N_{\mathbf{q}j} + \frac{1}{2}\right) + \frac{3}{2} \hbar\omega. \end{aligned} \quad (2.4)$$

Let us examine the transition to the dissociated state of the F' center. The wave function of the system which corresponds to the final state will then be written as follows:

$$\Psi_{\mathbf{n}, \dots, \mathbf{n}_2, \dots, N_{\mathbf{q}j}} = \Psi_{\mathbf{n}}(|\mathbf{r}_1 - \xi|) \Psi_{\mathbf{F}}(r_2) \varphi_{\mathbf{n}}(\xi) \prod_{\mathbf{x}} \Phi_{\mathbf{n}_x}(q'_x - r_x) \eta(\dots N_{\mathbf{q}j} \dots)$$

and the energy, correspondingly, as

$$\begin{aligned} E_{\mathbf{n}, \dots, \mathbf{n}_2, \dots, N_{\mathbf{q}j}} &= I_{\mathbf{F}} + I_{\mathbf{P}} + \hbar\omega \sum_{\mathbf{x}} \left(n'_{\mathbf{x}} + \frac{1}{2}\right) \\ &+ \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j} \left(N'_{\mathbf{q}j} + \frac{1}{2}\right) + E_{\mathbf{n}}^{(1)}. \end{aligned} \quad (2.6)$$

$\tilde{\Psi}_{\mathbf{n}}(|\mathbf{r}_1 - \xi|)$ and $\tilde{\Psi}_{\mathbf{F}}(r_2)$ in (2.5) are detailed wave

functions of electrons in the F-center and in the polaron; $\varphi_{\mathbf{n}}(\xi)$ is the wave function of the free polaron and $q_{\mathbf{x}\mathbf{F}}$ is the equilibrium position of the lattice coordinate, at which the adiabatic potential of the ground state of the F-center has a minimum. $I_{\mathbf{P}}$ and $I_{\mathbf{F}}$ in (2.6) are minimum values of the adiabatic potentials of the polaron and the F-center; $E_{\mathbf{n}}^{(1)}$ is the kinetic energy of the polaron. The third and fourth terms in (2.6) represent the energy of free longitudinal optical and acoustical lattice vibrations.

Let us now calculate the matrix element of operator (2.1). After transformations similar to those shown in ref. 12, we obtain

$$\begin{aligned} & \sum_{j=1}^3 \int \Psi_{\mathbf{F}}(r_2) \Psi_{\mathbf{F}}(|\mathbf{r}_1 - \xi|) [(l_{\mathbf{q}j} \nabla \mathbf{w}(r_1)) e^{i\mathbf{q}\mathbf{r}_1} + (l_{\mathbf{q}j} \nabla \mathbf{w}(r_2)) e^{i\mathbf{q}\mathbf{r}_2}] \\ & \times \Psi_{\mathbf{F}'}(r_1) \Psi_{\mathbf{F}'}(r_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{2iq}{3} M_{\mathbf{q}}(\xi), \end{aligned} \quad (2.7)$$

where

$$M_{\mathbf{q}}(\xi) = A_0 \tilde{I}_{\mathbf{q}}(\xi) + A_{\mathbf{q}} I_0(\xi); \quad (2.8)$$

$$\tilde{I}_{\mathbf{q}}(\xi) = \int \Psi_{\mathbf{F}}(|\mathbf{r} - \xi|) \Psi_{\mathbf{F}}(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}; \quad A_{\mathbf{q}} = \int \Psi_{\mathbf{F}}(\mathbf{r}) \Psi_{\mathbf{F}}(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} d\mathbf{r};$$

$$I_0(\xi) = \int \Psi_{\mathbf{F}}(|\mathbf{r} - \xi|) \Psi_{\mathbf{F}}(\mathbf{r}) d\mathbf{r}; \quad A_0 = \int \Psi_{\mathbf{F}}(\mathbf{r}) \Psi_{\mathbf{F}}(\mathbf{r}) d\mathbf{r}; \quad (2.9)$$

G is the Bethe-Sommerfeld constant.¹⁰ As can be seen in expression (2.7), the matrix element is different from zero only in the case of longitudinal acoustical waves, when $\mathbf{l}_{\mathbf{q}j} \parallel \mathbf{q}$. In future, we will omit the subscript j .

Using known properties of the operators for the annihilation and creation of $a_{\mathbf{q}j}$ and $a_{\mathbf{q}j}^*$, we obtain the following expression for the matrix element:

$$\begin{aligned} & \langle \mathbf{n}, N'_{\mathbf{q}} \dots n'_x | \hat{W} | \mathbf{n}, \dots N_{\mathbf{q}} \dots n_x \dots \rangle = \frac{2iG}{3} \sqrt{\frac{\hbar}{2\rho L^3}} \sum_{\mathbf{q}} \frac{q}{\omega_j} \\ & \times \langle \mathbf{k} | M_{\mathbf{q}}(\xi) | \mathbf{n} \rangle \left(\sqrt{N'_{\mathbf{q}} + 1} b_{N'_{\mathbf{q}}+1, N_{\mathbf{q}}} \right. \\ & \left. + \sqrt{N_{\mathbf{q}}} b_{N_{\mathbf{q}}-1, N_{\mathbf{q}}} \right) \prod_{j \neq \mathbf{q}} b_{N_{\mathbf{q}j} N_{\mathbf{q}j}} \prod_{\mathbf{x}} S_{\mathbf{n}_x \mathbf{n}_x}. \end{aligned} \quad (2.10)$$

where

$$\langle \mathbf{k} | M_{\mathbf{q}}(\xi) | \mathbf{n} \rangle = \int \varphi_{\mathbf{n}}^*(\xi) [A_0 \tilde{I}_{\mathbf{q}}(\xi) + A_{\mathbf{q}} I_0(\xi)] \varphi_{\mathbf{n}}(\xi) d\xi, \quad (2.11)$$

$$S_{\mathbf{n}_x \mathbf{n}_x} = \int_{-\infty}^{\infty} \Phi_{\mathbf{n}_x}(q'_x - q_{\mathbf{x}\mathbf{F}}) \Phi_{\mathbf{n}_x}(q'_x - r_x) dq'_x. \quad (2.12)$$

The expression for the probability of transition to a dissociated state, averaged over the initial population values of the acoustical and optical phonons, is of the following form:

$$P_{\mathbf{n}\mathbf{k}} = \frac{2\pi}{\hbar} \text{Av} \sum_{\dots N'_{\mathbf{q}} \dots} \sum_{\dots \mathbf{n}_x \dots} |\langle \mathbf{k} | \hat{W} | \mathbf{n} \rangle|^2 \delta(E_{\mathbf{k}} - E_{\mathbf{n}}), \quad (2.13)$$

where

$$E_{\mathbf{k}} - E_{\mathbf{n}} = m_0 \hbar\omega + \hbar\omega \sum_{\mathbf{x}} (n'_{\mathbf{x}} - n_{\mathbf{x}}) + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} (N'_{\mathbf{q}} - N_{\mathbf{q}}) + E_{\mathbf{k}}^{(1)}, \quad (2.14)$$

$$m_0 = \frac{I_{\mathbf{F}} + I_{\mathbf{P}} - I_{\mathbf{F}'} - \frac{3}{2} \hbar\omega}{\hbar\omega} \quad (2.15)$$

(Av designates the abovementioned averaging).

The averaging and the summation over the quantum numbers of the oscillators of phonon fields is effected with the help of a density matrix. The calculation, completely similar to that made in ref. 7, gives

$$P_{sk} = \frac{4\pi G^2}{9\hbar^2 p L^3 \omega} \left[\sum_q \frac{|\langle k | M_q(\xi) | n \rangle|^2}{\omega_q} (2N_q + 1) \right] \times \left\{ (N_q + 1) e^{\frac{-l+\beta}{2}} I_{l+}(z) \sum_{n=-\infty}^{\infty} \delta(n-l_+) + N_q e^{\frac{-l-\beta}{2}} I_{l-}(z) \sum_{n=-\infty}^{\infty} \delta(n-l_-) \right\}, \quad (2.16)$$

where

$$l_{\pm} = m_0 + \frac{E_k^{(1)}}{\hbar\omega} \pm \frac{\omega_q}{\omega}; \quad (2.17)$$

$$N_q = \left(\exp \frac{\hbar\omega_q}{k_0 T} - 1 \right)^{-1}; \quad (2.18)$$

$I_{\pm}(z)$ is a Bessel function of the imaginary argument

$$z = \frac{a_{F'}}{2 \operatorname{sh} \frac{\beta}{2}}; \quad (2.19)$$

$a_{F'}$ is the constant of the optical transition, where

$$a_{F'} = \sum_x [q_{x_{F'}} - (q_{x_F} + q_{x_0})]^2. \quad (2.20)$$

One can simplify (2.16) by assuming that $\omega_q/\omega \ll m_0$

$$P_{sk} = \frac{4\pi G^2}{9\hbar^2 p L^3 \omega} \left[\sum_q \frac{|\langle k | M_q(\xi) | n \rangle|^2}{\omega_q} g^2 (2N_q + 1) \right] \times \exp \left(-\frac{a_{F'}}{2} c \hbar k \frac{\beta}{2} + \frac{l\beta}{2} \right) I_s(z) \sum_{n=-\infty}^{\infty} \delta(n-e). \quad (2.21)$$

From (2.14), using (2.15), we obtain

$$k^2 = u_0^2 (l - m_0), \quad (2.22)$$

where

$$u_0^2 = \frac{2M\omega}{\hbar}. \quad (2.23)$$

In order to find the total probability of thermal ionization, it is necessary to integrate expression (2.21) for all states of the continuous spectrum, that is,

$$P_{\text{therm.}} = \int P_{sk} \delta(k) dk = \frac{L^3}{2\pi} \int P_{sk} k u_0^2 dl = \frac{4G^2 M}{9\pi^2 \hbar^2} \sum_{l \geq 0} e^{-\left(\frac{a_{F'}}{2} \operatorname{cth} \frac{\beta}{2} + \frac{l\beta}{2}\right)} \times I_s(z) \sum_q \frac{g^2 |\langle k | M_q(\xi) | n \rangle|^2}{\omega_q} (2N_q + 1). \quad (2.24)$$

In the general case it is not possible to make a summation with respect to q in (2.24). We will therefore consider the particular case of moderately low temperatures, that is,

$$\frac{\hbar\omega_q}{k_0 T} \ll L$$

$$\frac{\omega_q}{\omega} \ll \frac{1}{\beta}, \quad N_q \approx \frac{k_0 T}{\hbar\omega_q}. \quad (2.25)$$

Then

$$\sum_q \frac{|\langle k | M_q(\xi) | n \rangle|^2}{\omega_q^2} (2N_q + 1) \approx \frac{2k_0 T}{\hbar^2 c_a^2} \int \int \varphi_k^*(\xi') \varphi_n(\xi') \varphi_n(\xi) \times \left[A_0^2 \int \Psi_P(|r-\xi'|) \Psi_P(|r-\xi|) \Psi_{F'}^2(r) d\tau + A_0 I_0(\xi) \int \Psi_P(|r-\xi'|) \Psi_{F'}^2(r) \Psi_{F'}(r) d\tau \right]$$

$$+ A_0 I_0(\xi') \int \Psi_P(|r-\xi|) \Psi_{F'}^2(r) d\tau + I_0(\xi') I_0(\xi) \int \Psi_{F'}^2(r) \Psi_{F'}^2(r) d\tau \Big] d\tau_{\xi}. \quad (2.26)$$

If it is taken into account that $\Psi_{F'}^2(r)$, a rapidly decaying function, is combined with comparatively smooth functions, it is safe to replace the functions Ψ_P and Ψ_F by their values at $r=0$, that is,

$$\sum_q \frac{|\langle k | M_q(\xi) | n \rangle|^2}{\omega_q^2} g^2 (2N_q + 1) \approx \frac{2\omega L^3}{\beta C_a^2} [A_0^2 |A_0'|^2 + A_0 A A_0' A_1' + A_0 A A_0' A_0'^* + A_1^2 |A_1'|^2], \quad (2.27)$$

where

$$A_0 = \int \Psi_F(r) \Psi_{F'}(r) d\tau;$$

$$A_1' = \int \varphi_k(\xi) I_0(\xi) \varphi_n(\xi) d\tau_{\xi}; \quad A = \int \Psi_F(r) \Psi_{F'}^2(r) d\tau;$$

$$A_0' = \int \varphi_k(\xi) \varphi_n(\xi) \Psi_0(\xi) d\tau_{\xi}; \quad A_1^2 = \int \Psi_{F'}^2(r) \Psi_{F'}^2(r) d\tau. \quad (2.28)$$

C_a in Eq. (2.27), is the velocity of longitudinal sound waves which is connected with the modulus of elasticity by the relationship

$$C_a^2 = \frac{c_{11}}{\rho}. \quad (2.29)$$

The terms of the summation with respect to "l" decrease rapidly in (2.24), because $m_0 \gg 1$, so that the whole sum is approximated sufficiently accurately by the first term. Then

$$\frac{P_{\text{therm.}}}{\omega} = Q \beta^{-1} \exp \left(-\frac{a_{F'}}{2} \operatorname{cth} \frac{\beta}{2} - \frac{l\beta}{2} \right) I_s(z), \quad (2.30)$$

where it is necessary to take "e" as the integer closest to m_0 ($e \geq m_0$) and

$$Q = \frac{4MG^2 L^3 k}{9\pi^2 \hbar^2 c_{11}} [A_0^2 |A_0'|^2 + A_0 A (A_0' A_1' + A_0' A_1'^*) + A_1^2 |A_1'|^2]. \quad (2.31)$$

Turning to the calculation of the parameter Q , we will select our electronic wave functions in the form¹¹

$$\Psi_F(r) = \frac{a_F^{3/2}}{\sqrt{\pi}} e^{-a_F r}; \quad \Psi_{F'}(r) = \frac{a_{F'}^{3/2}}{\sqrt{\pi}} e^{-a_{F'} r}; \quad \Psi_P(r) = \frac{a_P^{3/2}}{\sqrt{\pi}} e^{-a_P r}. \quad (2.32)$$

We will select the polaron wave function of the continuous spectrum as a plane wave

$$\varphi_k(\xi) = \frac{1}{L^{3/2}} \exp(ik\xi). \quad (2.33)$$

If the integrals (2.28) are calculated with the help of wave functions (2.32), (1.3), (2.33) Q will be equal to

$$Q = \frac{47 \left(\frac{M}{\mu} \right) \hbar \omega g \beta^2 k}{4.5 \pi^2 A (\gamma + \gamma_1)^3} \left\{ \frac{(\gamma \gamma_1) z_1^2}{(\gamma + \gamma_1)^2 (z_1^2 + k^2)^4} + \left[\frac{2(\gamma \gamma_1)^3 z_1}{(\gamma_1^2 - 1)^3 (z_1^2 + k_1^2)^2} + \frac{\gamma_1^6}{(\gamma_1^2 - 1)^6} \right] \times \left[\frac{z_1 (\gamma_1^3 - \gamma_1)}{(z_1^2 + k_1^2)^2} - \frac{2\gamma_1}{a_{P_1} (z_1^2 + k_1^2)} + \frac{z_2 (\gamma_1^2 - 1)}{(z_2^2 + k_1^2)^2} + \frac{2\gamma_1}{a_{P_1} (z_2^2 + k_1^2)} \right] \right\}$$

In the last formula we changed over to the dimensionless units $\alpha_{P_1} = \alpha_P d$, $\alpha_{F_1} = \alpha_F d$, $\alpha_{F'_1} = \alpha_{F'} d$, $\beta_1 = \beta d$, $k_1 = kd$, $z_1 = \alpha_{P_1} + \beta_1$, $z_2 = \alpha_{F_1} + \beta_1$, and introduced the designations $c' = 2c - (1/n^2)$,

$$g = \frac{G^2 a_F^3}{\hbar d^3 \omega c_F}, \quad \gamma = 1 + \frac{16}{5\epsilon c}, \quad \gamma_1 = \frac{c'}{c} \left(1 + \frac{16}{5\epsilon c'}\right), \quad (2.35)$$

$$d = \frac{\hbar^2 \epsilon}{\mu e^2}, \quad A = \frac{\mu e^4}{2\hbar^2 \epsilon^2}, \quad (2.36)$$

with M being the effective mass of the polaron.

A numerical calculation of Q_ω values was made for KCl and for NaCl crystals for parameter values taken from ref. 9. (The parameter g is taken from ref. 6.) It was found that

$$Q_\omega(\text{KCl}) = 8.2 \cdot 10^{18} \text{ sec.}^{-1}, \quad Q_\omega(\text{NaCl}) = 2.4 \cdot 10^{18} \text{ sec.}^{-1},$$

the value $a_{F'}$ being calculated by means of Eq. (3.4) of ref. 8. An asymptotic formula was used for large index Bessel functions

$$I_0(z) \approx (2\pi \sqrt{z^2 + e^2})^{-1/2} \exp\left(\sqrt{z^2 + e^2} - e \operatorname{arcsch} \frac{e}{z}\right). \quad (2.37)$$

It should be pointed out that the temperature dependence of the thermal dissociation probability of an F' -center (2.30) is not exponential at temperatures at which F' -centers do not exist in alkali halide crystals. The exponential dependence arises at temperatures well above room temperature. All F' -centers are, however, dissociated at temperatures above room temperature, as is well known from experiment.¹³

Let us examine the room temperature range ($\beta = 1$). In this case undissociated F' -centers still remain in alkali halide crystals; furthermore, inequality (2.25) is also fulfilled. As a result of a calculation using formula (2.30), we obtain for the thermal dissociation probability of F' -centers

$$P_{\text{therm.}}(\text{NaCl}) = 7 \cdot 10^{12} \text{ sec.}^{-1}, \quad P_{\text{therm.}}(\text{KCl}) = 5 \cdot 10^{10} \text{ sec.}^{-1}.$$

The thermal ionization probability of an F' -center is thus much larger than that of an F -center. This fact is corroborated by experiment: F' -centers dissociate faster than F -centers. It must be kept in mind, however, that the use of a plane wave as a function of the continuous spectrum increases the transition probability, as shown in ref. 6.

It would be interesting to evaluate the effective capture cross section of a polaron by an F -center. It is not difficult to establish a connection between the capture probability and the thermoionization probability from the principle of detailed balancing:

$$P_{\text{capt.}} = \rho \exp\left(\frac{w_{F'}}{k_0 T}\right) P_{\text{therm.}}, \quad (2.38)$$

where ρ is the Maxwellian normalizing factor and $w_{F'}$

is the thermal dissociation energy of the F' -center. Taking (2.38) into account, we obtain the following expression for the effective capture cross section:

$$\sigma = \frac{\hbar^3 \exp\left(\frac{w_{F'}}{k_0 T}\right) \cdot P_{\text{therm.}}}{2\pi \sqrt{6\pi M} (k_0 T)^2}. \quad (2.39)$$

For $\beta = 1$, (2.39) gives

$$\sigma(\text{NaCl}) \approx 3 \cdot 10^{-14} \text{ cm}^2, \quad \sigma(\text{KCl}) \approx 6.2 \cdot 10^{-15} \text{ cm}^2.$$

The experimental value of the effective capture cross section in KCl cited in ref. 11 is of the same order of magnitude as that calculated above.

In conclusion, I take the opportunity to thank Mr. Yu. E. Perlin for suggesting this problem, and for his constant help in solving it.

REFERENCES

1. Hyang Kyn and A. Rhys, *Proc. Roy. Soc.* **204**, 406 (1950).
2. R. Kubo, *Phys. Rev.* **86**, 929 (1952).
3. H. D. Vassileff, *Phys. Ref.* **96**, 603 (1954).
4. Yu. E. Perlin and M. M. Sharand, *Uchenye Zapiski Kishinevskogo Univ., Ser. Fiz.* **24**, 41 (1956).
5. V. A. Kovarskii, *Uchenye Zapiski Kishinevskogo Univ., Ser. Fiz.* **17**, 185 (1955).
6. Yu. E. Perlin, *Fiz. Tverd. Tel. Soviet Phys.-Solid Steel* **11**, 243 (1960).
7. Yu. E. Perlin, *Opt. i Spekt.* **8**, 386 (1960), *Optics and Spectroscopy* **8**, 199 (1960).
8. A. G. Cheban, *Uchenye Zapiski Kishinevskogo Univ., Ser. Fiz.* **55**, 183 (1960).
9. S. I. Pekar and O. F. Tomasevich, *Zhur. Eksptl. i Teoret. Fiz.* **21**, 11 (1951).
10. G. Bethe and A. Sommerfeld, "Elektronnaya teoriya metallov" (Electron Theory of Metals). Ob'ed. Nauch.-Tekh. Izd., Moscow, 1938.
11. S. I. Pekar, "Issledovaniya po elektronnoi teorii kristallov. Gosudarst. Izd. Tekh.-Teoret. Lit., Moscow, Leningrad, 1950.
12. Yu. E. Perlin, *Zhur. Eksptl. i Teoret. Fiz.* **21**, 547 (1951).
13. H. Pick, *Nuovo Cimento* **7**, 498 (1958).
14. N. F. Mott and R. V. Gurney, "Elektronnye protsessy v ionnykh kristallakh" (Electronic Processes in Ionic Crystals). Gosudarst. Tekh. Izd., Moscow, 1950. 2nd ed., Oxford Univ. Press, 1948.

DETAILS OF THE MECHANISM OF PHOSPHORESCENCE STIMULATED BY LIGHT FROM THE F-BAND REGION

I. A. Parfianovich and E. I. Shuraleva (pp. 500-504)

Received 30 May 1960

The decay of the phosphorescence of NaCl-Ni phosphors with different activator concentrations was studied. It was shown that the probability of recombination of free electrons with hole centers varies during the liberation of the stored light sum.

It is well known that the afterglow processes in crystal phosphors are complex in nature. In describing the kinetics of the afterglow associated with the release of electrons from trapping centers, both the complex nature of the trapping level spectrum and the relationship between the recombination probability and repeated electron trapping is taken into account. In the theory of the kinetics it is assumed that the brightness of the afterglow is expressed by the following relationship:

$$I = \alpha ANn, \quad (1)$$

where n is the concentration of hole centers with which the free electrons recombine, N is the concentration of electrons in the conduction band, An is the recombination probability per unit time, and α is the factor taking account of the efficiency of the process with regard to luminescence. In Eq. (1) A is considered a constant independent of time.

However, it must be noted that this approach to the theoretical description of the kinetics of the afterglow is inadequate, since experimental data show that A may change during the release of the stored light sum. We were led to this conclusion by experiments on the decay of phosphorescence in NaCl-Ni phosphors with different activator concentrations. Figure 1 gives the results of these experiments, showing the change in the relative brightness of the phosphorescence (I/I_0) when the NaCl-Ni phosphors are illuminated with light from the F-band region (F-light). The experiment was conducted at room temperature, while the initial concentration of F-centers was approximately the same for all the specimens. Curve 1 refers to the crystal with the greatest activator content, curve 4 to that with the least. We will not give data on the absolute activator concentrations, but we may remark that the changes in concentration in going from one speci-

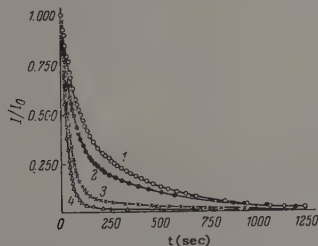


Fig. 1. Decay of phosphorescence in NaCl-Ni phosphors (Nos. 1 to 4) with different activator concentrations. The numbers on the curves correspond to the crystal numbers in the Tables. Curve 1 refers to the crystal with the greatest activator concentration, curve 4 to that with the least.

Table 1. The Degree of Optical Destimulation of NaCl-Ni Phosphors with Different Activator Concentrations

Crys- tal No.	K_{246} (cm^{-1})	S_{opt} (after 20 min)	S_T (resid- ual)	$\frac{S_T}{S_{\text{opt}}}$
1	8.80	410	20	0.05
2	8.48	297	35	0.12
3	2.20	116	83	0.71
4	0.50	43.6	113.5	3.10

men to another can be estimated from the data on the absorption coefficient at the maximum of the activator band, presented in Table 1. Referring to the initial stage in the decay curves of Fig. 1, we see that the phosphor with the least activator concentration has the greatest reduction in brightness.

It should be noted that no parallel is observed between this effect and the rate of destimulation of the stored light sum, as Table 1 shows. The first column of Table 1 gives the crystal numbers, corresponding to the numbers of the curves in Fig. 1; the second column gives the absorption coefficient K at the maximum of the activator band ($\lambda_{\text{max}} = 246 \text{ m}\mu$), the third the optical light sum S_{opt} obtained with destimulation with light from the F-band for 20 min, the fourth the light sum S_T remaining after optical destimulation, as measured by subsequent thermal destimulation, and the fifth gives the ratio S_T/S_{opt} , between this residual light sum and the optical light sum.

We see from these data that as the activator concentration is reduced the optically destimulated light sum becomes a smaller fraction of the total light sum stored in the phosphor.

At room temperature the phosphorescence is accompanied by trapping of the electrons, released by the light from the F-levels, at shallower trapping levels M and F' . To obtain phosphorescence which is not complicated by this secondary trapping, we carried out experiments at $T \approx 70^\circ\text{C}$ (at this temperature the M -centers become unstable and the F' -centers are not formed). Figure 2 shows two curves relating to the same phosphor, optically destimulated at different temperatures. Curve 1 shows the change in brightness of the phosphorescence at room temperature, curve 2 at 70°C . Comparing the shapes of these two curves, we see that the decay of the phosphorescence occurs more slowly at the higher temperature.

This behavior was successfully explained by study of the interrupted action of destimulating light on an excited phosphor. As one of us has shown,¹ under these conditions a rise in the brightness of the phosphores-

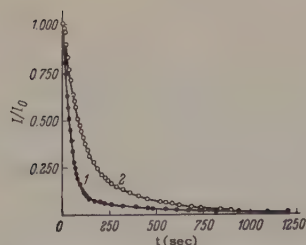


Fig. 2. Decay of phosphorescence in NaCl-Ni crystal No. 3. Curve 1—at room temperature; curve 2—at 70°C.

cence is observed. This phenomenon is quite general and is observed in alkali halide phosphors with different bases and activators. To study the mechanism of the rise in brightness of the phosphorescence with interrupted destimulating light, we used the same specimens as in the study of the decay of the phosphorescence. Figure 3 (a,b) shows, for example, the results for two crystals with different activator contents (the activator concentration was varied approximately fourfold). After a definite fraction of the stored light sum, identical for all the specimens, had been destimulated (Fig. 3), the action of the destimulating light was interrupted (t_1). During the dark interval the crystal was heated to destroy the M-centers which had been formed during the action of the F-light. After this, the crystal was cooled and at time t_2 was again subjected to the destimulating light, which then acted up to time t_3 . It is easily seen that the brightness at the start of the second phosphorescence considerably exceeds that at time t_1 . This effect can be observed repeatedly as is shown in the same figure at time t_4 , when only a short pulse of destimulating light was applied. Comparing Figs. 3a and 3b we see that the size of the increase in the repeated phosphorescence depends on the activator concentration; where the concentration is lower (Fig. 3a) the effect is greater.

Together with the measurement of the brightness of the phosphorescence each time before and after applying the destimulating light, a measurement was made of the absorption coefficient at the maxima of the F- and M-bands. The results of these experiments are shown in Table 2, which shows the absorption coefficients at the maxima of the F-band (K_F) and the M-band (K_M), and also the brightness of the phosphorescence I for all the crystals at times t_0 , t_1 , and t_2 , corresponding to the times shown in Fig. 3. The data of Fig. 2 were used to

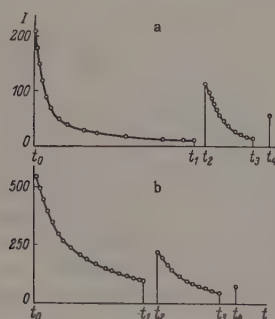


Fig. 3. Change in the brightness of the phosphorescence of NaCl-Ni phosphors (a) No. 4 and (b) No. 1, under the interrupted action of destimulating light.

Table 2. Change in the Values of K_F , K_M , and I with Interrupted Action of F-light

Crystal No.	1			2			3			4		
	K_F	K_M	I	K_F	K_M	I	K_F	K_M	I	K_F	K_M	I
t_0	0.538	0.032	545	0.580	0.031	550	0.465	0.019	496	0.451	0.020	485
t_1	0.202	0.023	95	0.236	0.027	91	0.185	0.022	29	0.189	0.033	17
t_2	0.145	0.012	220	0.160	0.012	272	0.155	0.012	272	0.143	0.020	285

form Table 3, which gives results characterizing the relative changes of the quantities. The subscript 0 is used to show values corresponding to time t_0 , subscript 1 for time t_1 , and subscript 2 for time t_2 . This table shows that with optical destimulation the fraction of the F-centers destroyed is approximately the same in all cases (column 2). With regard to the M-bands, a different situation is found. For the first two crystals (column 3) this band is weakened by the action of the F-light and in the two following ones (with lower concentration) it increases. Simultaneously, a considerable reduction in the brightness of the phosphorescence (column 4) is observed, the less the nickel content of the phosphors, the greater the reduction. In addition, percentage-wise, the reduction which occurs in the brightness of the phosphorescence is considerably greater than the change in the concentration of the F-centers.

Table 3. Relative Changes in the Values of K_F , K_M , and I for Interrupted Action of the Destimulating Light

Crystal No.	$\frac{K_F^1}{K_F^0}$	$\frac{K_M^1}{K_M^0}$	$\frac{I_1}{I_0}$	$\frac{K_F^2}{K_F^1}$	$\frac{K_M^2}{K_M^1}$	$\frac{I_2}{I_1}$
1	0.38	0.72	0.17	0.72	0.52	2.3
2	0.41	0.87	0.16	0.68	0.45	3.0
3	0.40	1.15	0.06	0.84	0.55	9.4
4	0.42	1.65	0.03	0.76	0.61	16.8

During the heating of the crystal to 70°C after the optical destimulation, a further reduction in the number of F- and M-centers occurs, varying little in amount among the different crystals (columns 5 and 6). At the same time the brightness of the succeeding phosphorescence after heating increases for all the crystals (column 7). This effect, as we noted above, is greater, the smaller the activator concentration in the phosphor. On the other hand, it is directly related to the presence and the behavior of M-centers: firstly, the reduction in brightness of the phosphorescence during the time $t_1 - t_0$ occurs more rapidly in the case where the number of M-centers increases under the action of the F-light, and secondly, in this same case, after partial dissipation of the M-centers, the greatest increase of the phosphorescence occurs after heating.

All this shows that one of the reasons for the change in brightness of the phosphorescence under the action of the destimulating light is the presence of M-centers in the phosphor and their stability relative to light from the F-band region. This effect of the M-centers can be understood only if it is supposed that the distribution of both the luminescence activator centers and the electron trapping centers are nonuniform. It is interesting that Compton and Klick² concluded that the distribution of R-, M-, and N-centers was not random, on the basis of the change in the absorption spectrum of colored NaCl crystals when they are illuminated at 77 and 4°K.

Therefore, it can be concluded from what has been

said that in alkali halide crystals there are certain regions in which activator concentrations and trapping centers of type M predominate. When free electrons are present in the crystal the M-levels fill up. As the electrons accumulate at these levels, a peculiar screening of the ionization centers of the luminescence occurs, leading to a more rapid reduction in brightness than would occur if there were no obstacle to the recombination processes.

Since experiment shows that in NaCl-Ni phosphors with low nickel content the number of M-centers increases with optical decay of the F-centers, it becomes comprehensible from this fact how in these crystals the decay of the phosphorescence occurs considerably more rapidly than in crystals with large activator concentrations, where the M-centers become unstable with respect to F-light. For this same reason there is a fall in the rate of reduction of the brightness of the phosphorescence observed as the temperature rises, since in this case the F-centers are not formed (Fig. 2). It must be emphasized that, in contrast to the optical destimulation at room temperature, where complete release of the stored light sum does not occur, here, as the experiment shows, the phosphor can be completely destimulated by light. Therefore, the presence of electrons at the M-levels also determines the degree of optical destimulation of the phosphors.

Summarizing, we may say that the probability of re-

combination of free electrons with hole centers changes during the optical destimulation of the phosphors. It becomes smaller, the more M-centers form in the regions where the luminescence centers are located. Consequently, the decay of the phosphorescence must be related not only to the change in the quantities n and N (Eq. 1) but also to the degree by which A is reduced. Therefore, in describing the kinetics of the afterglow, the fact that the quantity A may change during the release of the stored light sum must be taken into account. In particular, in optical destimulation of the light sum stored at the F-levels it falls in proportion to the accumulation of electrons at the M-levels and rises as the M-centers dissipate, reaching a maximum in conditions where the M-centers are completely dissipated.

This behavior of the quantity A , arising from the physical causes discussed here, can explain both the features of the decay of the phosphorescence in phosphors with different activator contents and the effect of the rise in brightness of the phosphorescence under interrupted action of the destimulating light.

REFERENCES

1. I. A. Parfianovich, *Opt. i Spektr.* **2**, 392 (1957).
2. W. Compton and C. Klick, *Phys. Rev.* **112**, 1620 (1958).

DEPENDENCE OF YIELD AND OTHER OPTICAL PROPERTIES OF ZINC SULFIDE PHOSPHORS ON THE SIZE OF UNCRUSHED CRYSTALS*

*The present paper, which is devoted to a study of the effect of size on the luminescent properties of natural ZnS crystals, serves as the introduction to a series of papers dealing with the effect of mechanical crushing on the luminescence of crystals.

V. L. Levshin and B. D. Ryzhikov (pp. 505-511)

Received 26 May 1960

The brightness of luminescence is shown to decrease rapidly with a decrease in the linear dimensions of uncrushed ZnS phosphor crystals. This decrease in brightness can be only partially explained by an increase in scattering; it is also caused by a direct decrease in yield. Crystals of different sizes exhibit certain differences in their emission spectra and glow curves. The temperature dependence of the brightness of luminescence also varies.

INTRODUCTION

Mechanical crushing of crystalline phosphors of the zinc sulfide type decreases their photoluminescent brightness. This phenomenon, called triboquenching, has been known a long time;¹ however, its exact cause has not yet been determined.

Mechanical crushing decreases particle size. This results in an increase in the scattering of both the exciting and the luminescent light. A number of authors believe that scattering accounts for the decrease in the luminescent brightness of mechanically crushed phosphors. This supposition was first stated by Riehl and Ortman.² While these authors do not deny the possibility that crushing may cause a certain decrease in luminescence yield, they assert that the decrease in brightness occurring when the crystals are crushed is mainly caused by a change in the dispersion of particle size, and hence by an increase in scattering.

As far as scattering is concerned, the method of obtaining the fine powder is immaterial, whether by grinding or in preparing the crystalline phosphor. Brightness measurements of uncrushed powders of different degrees of dispersion are therefore of direct interest. Fonda³ found a decrease in the intensity of luminescence of willemite when the grain size was reduced below 5μ . In his experiments, however, the brightness of the phosphors might have been affected not only by crystal size but also by a change in baking temperature.

In studying the brightness of willemite as a function of particle size, Oldham and Kunert⁴ observed an increase in brightness when the particle size was reduced from 700 to 20μ . Bodo's article⁵ lists data on a decrease in the brightness of artificial apatite for particle sizes below 10μ . Thus light scattering results in a brightness decrease only for crystal sizes below 10μ . However, even within these limits, the decrease in brightness is hardly caused by scattering alone. The hypothesis of

Riehl and Ortman runs into serious difficulties in trying to explain the sharp difference in the magnitude of quenching of phosphors with different hosts, the degree of triboquenching as a function of wavelength, etc. For many phosphor types, the decrease in brightness observed experimentally is much greater than could be ascribed to a change in particle size.

Later work⁶⁻⁹ revealed the existence of other effects which decrease the brightness of crystalline phosphors which are crushed mechanically. Frey⁶ assumed that the main cause of triboquenching in zinc sulfide phosphors is the transition from wurtzite to sphalerite occurring in the crushing process. On the basis of the connection which they found between the decrease in luminescent brightness and the broadening of lines in the Debye diagram, Veits and one of the present authors⁷ concluded that the presence of residual deformation in fractured crystals is the main cause of triboquenching. In a more concrete discussion of the effect of deformation, Broser and Reichardt⁸ indicate that when the structure of the crystalline lattice is disrupted, a system of deep trapping levels may be formed, from which nonradiative transitions are possible. In the opinion of these authors, this is the cause of the decrease in brightness. Klement and Gindina⁹ have ascertained that in alkali halide phosphors there is a decomposition of the solid solution consisting of host and activator. They assume this to be the main cause of the decrease in the brightness of luminescence.

The various above-mentioned effects which accompany the crushing of crystals, and which affect the brightness of phosphor luminescence, cannot be summarily dismissed. Papers continue to appear, however, in which the decrease in brightness of luminescence after crushing is explained solely by a change in particle size,¹⁰ even though there are no theoretical calculations in the Riehl and Ortman paper and the experiment is carried out on a very limited scale.

In recent years we have carried out a series of investigation on the changes in various properties of ZnS phosphors caused by mechanical crushing. The present paper, the first one of this series, is devoted to a study of the change in the brightness of luminescence of infinitely thick layers of ZnS phosphors. These phosphors were not crushed, but have different degrees of the dispersion. We compare the experimental results obtained with the theoretical calculations of Stepanov and Chekalinskaya.¹¹⁻¹²

DESCRIPTION OF THE EXPERIMENT

The luminors obtained when a batch is baked usually consist of particles of different sizes. We used the settling method¹³ to obtain a monodisperse powder. The settling was carried out in cylinders, and was repeated 15 to 20 times. The particle size was determined from the Stokes formula. We shall henceforth specify the particle size by the average linear dimensions of the particles in the fractions investigated. We obtained a series of fractions whose characteristics are listed in the Table.

The brightness of an infinitely thick phosphor layer ($d \approx 2$ mm) was measured at the maximum of the emission

band. All optical measurements were carried out with an ISP-51, using a PS-381 exit collimator.

MEASUREMENT OF BRIGHTNESS AND LUMINESCENCE YIELD OF ZnS PHOSPHORS AS A FUNCTION OF CRYSTAL SIZE

Figures 1 (a-d) and 2 (a-d) contain curves which give the brightness of luminescence of an infinitely thick layer during excitation as a function of crystal size. These curves are given for ZnS, ZnS:Pb, ZnS:Mn, ZnS:Cu, and ZnS:Sm. The individual curves in Figs. 1 and 2 correspond to excitation by definite mercury lines: 312, 365, 405, and 436 m μ . In each series of samples having the same composition but different degrees of dispersion, we used the brightness of a particular fraction (usually the 27 μ fraction) as a reference standard for all types of excitation.

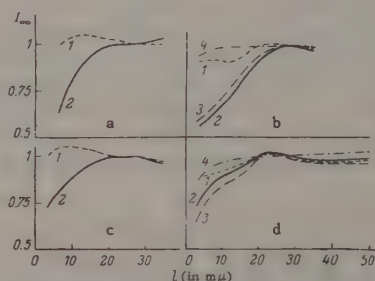


Fig. 1. Brightness of luminescence as a function of crystal size. a—ZnS; b—ZnS:Mn (10^{-3} gm/gm) (blue luminescence); c—ZnS:Mn (10^{-3} gm/gm) (orange luminescence); d—ZnS:Mn (3×10^{-2} gm/gm). λ_{exc} (in m μ): curves 1—312; curves 2—365; curves 3—405; curves 4—436.

The experimental curves indicate that there is a sharp drop in brightness only in the range of small crystal sizes. The initial decrease in crystal size (down to $\sim 20 - 10 \mu$) has little effect on the brightness. In some cases, it may even increase it.

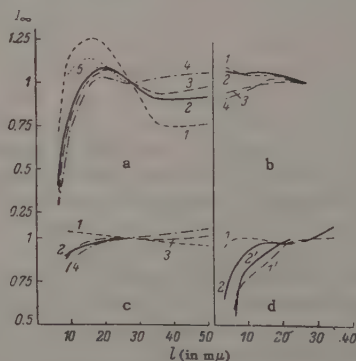


Fig. 2. Brightness of luminescence as a function of crystal size. a—ZnS:Cu (3×10^{-5} gm/gm); b—ZnS:Cu (10^{-4} gm/gm); c—ZnS:Cu (5×10^{-3} gm/gm); d—ZnS:Pb (5×10^{-3} gm/gm) (curves 1, 2), ZnS:Sm (curves 1', 2'). λ_{exc} (in m μ): curves 1, 1'—312; curves 2, 2'—365; curves 3—405; curves 4—436; curve 5—cathode ray excitation.

Fraction boundaries (μ)	60-40	40-30	30-24	24-20	20-15	15-10	10-7	7-5	5-1
Average linear particle size (μ)	50	35	27	22	17.5	12.5	8.5	6	3

A comparison of the individual curves in each figure indicates that their behavior depends very strongly on the method of excitation. As a rule, the decrease in brightness is more pronounced for excitation by weakly absorbed rays. Hence it is largely due to the scattering of luminescence, which increases with the thickness of the layer excited. A comparison of the individual figures also shows that the effect of a decrease in size depends strongly on phosphor composition and method of preparation.

Figure 3 contains theoretical curves for the variation of the quantity I/κ (where I is the intensity and κ the luminescence yield) for different values of the absorption coefficients k and k' of the exciting and luminescent light, respectively. The curves were taken from the paper by Chekalinskaya.¹² If κ is considered to be independent of crystal size, then the relative shape of these curves should reproduce that of the experimental curves in Figs. 1 and 2.

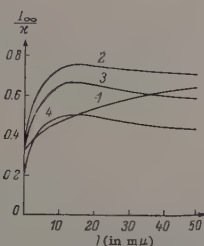


Fig. 3. Theoretical dependence of I/κ on crystal size (from ref. 12). Absorption coefficients (in cm^{-1}): curve 1— $k = 200$, $k' = 2$; curve 2— $k = 1000$, $k' = 1$; curve 3— $k = 1000$, $k' = 10$; curve 4— $k = 1000$, $k' = 100$.

A comparison of the curves of Figs. 1 and 2 with those of Fig. 3 shows a certain qualitative resemblance between them. Both the theoretical and the experimental curves exhibit a certain rise at the initial decrease in crystal size. This is followed by a sharp drop in brightness. The decrease in the effect of crystal size on the intensity of luminescence when the activator concentration is increased appreciably, and when strongly absorbed light is used for excitation, is also reflected in the theoretical curves.

The indicated resemblance is, however, only qualitative. A quantitative comparison of the curves in Figs. 1 and 2 with the curves of Fig. 3 reveals very serious discrepancies, which are of a nonaccidental nature. In a number of cases, the increase in brightness accompanying the initial decrease in crystal size proceeds much faster experimentally than would be expected from theory. (See, for example, Fig. 2a.) The subsequent drop in intensity starts much earlier experimentally than would be expected from theory, and proceeds much more rapidly. In particular cases (see, for example, the same Fig. 2a), the drop proceeds so rapidly that it results in the disappearance of luminescence for small crystals of respectable size. This does not follow from theory under any circumstances (for constant κ).

The indicated differences in the shapes of the curves in Figs. 1 and 2 on the one hand, and of the theoretical curves in Fig. 3 on the other, cannot be due to experimental error (e.g., in the determination of the average crystal size). Such errors can only cause a lack of smoothness in some of the curves (for example, Figs. 1c and 1d).

The large quantitative difference between the the-

oretical and experimental curves, and particularly the specific nature of the deviations for different phosphor types, naturally leads us to the conclusion that the yield κ varies with crystal size.

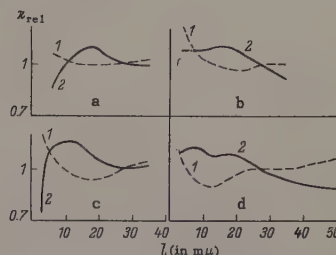


Fig. 4. Calculated values of $\kappa_{\text{rel.}}$ for particles of different size. a—ZnS; b—ZnS:Pb (5×10^{-3} gm/gm); c—ZnS:Mn (10^{-3} gm/gm) (blue luminescence); d—ZnS:Mn (3×10^{-2} gm/gm). $\lambda_{\text{exc.}}$ (in $\text{m}\mu$): curves 1—312; curves 2—365.

Figure 4 (a-d) contains curves characterizing the change in the relative values of κ as a function of crystal size. The values of κ were obtained by dividing the ordinates of the curves in Figs. 1 and 2 (i.e., the values of I) by the ordinates of the curves in Fig. 3 (i.e., by the quantity I/κ). Here

$$\frac{I}{I/\kappa_{\text{abs.}}} = a\kappa_{\text{abs.}}$$

where a is the proportionality factor between the values of I shown in Figs. 2 and 3, respectively, which were measured in different relative units. The behavior of the quantities $a\kappa_{\text{abs.}} = \kappa_{\text{rel.}}$ is shown in Fig. 4. The value of $\kappa_{\text{rel.}}$ is set at unity for all curves for 27μ crystals. We did not measure the spectral absorption coefficients for the samples investigated. Widely different values are listed for them in the literature: 5×10^{-4} and $13.5 \times 10^{-4} \text{ cm}^{-1}$ for k_{312} ,^{19,20} from 40 to 5000 cm^{-1} for k_{366} ,^{16-18,20} 100 cm^{-1} for k_{300} .²⁰ We chose values of k and k' which led to the smallest differences between theoretical and experimental brightness values and which at the same time, taking into account the coarseness of the experimental data, could be considered acceptable. Thus we used $k_{312} = 1000 \text{ cm}^{-1}$, $k_{366} = 200 \text{ cm}^{-1}$, and $k' = 10 \text{ cm}^{-1}$.

However, even with these values of k and k' , which were most favorable for theory, $\kappa_{\text{rel.}}$ was found to depend on crystal size. An examination of Fig. 4 indicates that the variation of $\kappa_{\text{rel.}}$ with crystal size proceeds differently for phosphors with different activators, as well as for each particular phosphor when excited by light of different wavelengths.

STUDY OF SPECTRA, GLOW CURVES, AND BRIGHTNESS AS A FUNCTION OF TEMPERATURE FOR UNCRUSHED CRYSTALS OF DIFFERENT SIZE

Figure 5 (a, b) shows the normalized emission spectra of individual fractions of ZnS and ZnS:Cu (3×10^{-5} gm/gm) phosphors, the brightness of the maximum of the principal emission band being chosen as unity. It is easily seen that the spectral characteristic of the blue band in the inherent luminescence of ZnS phosphors is the same for all fractions (Fig. 5, a). For ZnS:Cu (3×10^{-5} gm/gm) (Fig. 5, b) the intensity of the blue band ($445 \text{ m}\mu$) increases relatively to that of the green band ($525 \text{ m}\mu$) as the particle size decreases (27 , 17.5 , and 8.5μ). The

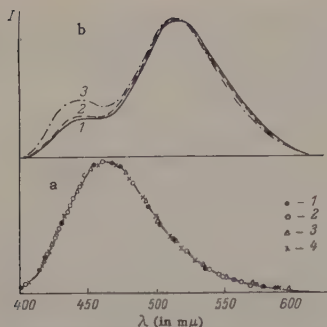


Fig. 5. Luminescence spectra of crystals of different size. a—ZnS: 1-27; 2-22; 3-12.5; 4-6 μ ; b—ZnS:Cu (3×10^{-5} gm/gm): curve 1-27; curve 2-17.5; curve 3-8.5 μ .

spectrum of the ZnS:Cu (10^{-4} gm/gm) phosphor also changes with a change in size. Figure 5 b shows that in addition to the relative increase in brightness of the blue band, there is a simultaneous small displacement of the spectra to the blue. This displacement increases with decreasing particle size. We may conclude that there may be certain structural differences between crystals of different sizes.

To ascertain the nature of the structural differences between crystals of different size, we studied the Debye diagrams of fractions of the ZnS:Cu (3×10^{-5} gm/gm) phosphor. We found that this phosphor consisted of a mixture of the wurtzite and sphalerite modifications. However, the Debye diagrams of fractions of different sizes turned out to be identical. Hence the change in the optical characteristics of the phosphors cannot be explained either by a change in the ratio of wurtzite to sphalerite by distortion of the crystalline lattice throughout the entire volume of the crystal. For crystals of different sizes, the structure of the lattice apparently varies only near the luminescence and capture centers. Such changes in lattice structure should cause certain changes in the structure of the centers themselves, but cannot be detected by x-ray structural analysis.

The difference in the structure of luminescence and capture centers in crystals of different size is also confirmed by changes in the glow curves and the brightness-

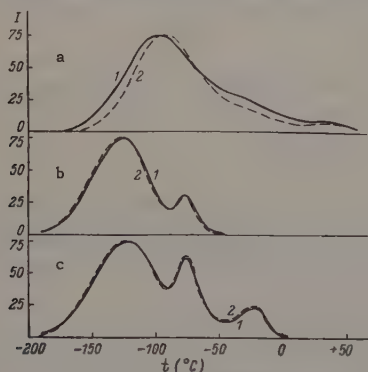


Fig. 6. Glow curves for crystals of different size. a—ZnS:Cu (3×10^{-5} gm/gm): curve 1-27; curve 2-8.5 μ ($\beta = 13^\circ/\text{min}$). b—ZnS:Mn (10^{-3} gm/gm) (blue luminescence): curve 1-22; curve 2-6 ($\beta = 12^\circ/\text{min}$). c—ZnS:Mn (10^{-3} gm/gm) (orange luminescence): curve 1-22; curve 2-6 ($\beta = 12^\circ/\text{min}$).

temperature characteristics (as well as by differences in emission spectra). Figure 6 (a, b, c) contains glow curves for ZnS:Cu (3×10^{-5} gm/gm) (green band) and for ZnS:Mn (10^{-3} gm/gm) (blue and orange bands). Glow curves of ZnS:Cu phosphors obtained for particles of various sizes exhibit a shift of the maxima toward higher temperatures when the crystal size diminishes (Fig. 6, a). The shift with crystal size in the positions of the blue and orange luminescence (Fig. 6, b and c, respectively) for ZnS:Mn (10^{-3} gm/gm) crystals is within the limits of experimental error. It should be noted that for this phosphor, the heights of the glow curve peaks are in the ratio of 1:0.4:0 for blue luminescence and 1:0.8:0.3 for orange luminescence. This confirms the data of refs. 14 and 15 which indicate that during thermal de-excitation, the electrons from the deep levels move predominantly toward manganese centers.

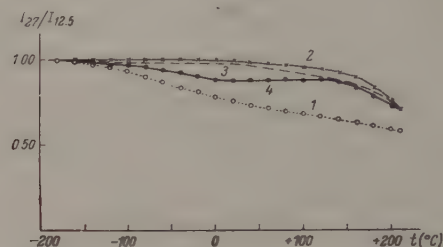


Fig. 7. Temperature dependence of the brightness ratio between 27 μ and 12.5 μ crystals for ZnS:Cu (3×10^{-5} gm/gm) phosphors. λ_{exc} (in m μ): curve 1-436; curve 2-405; curve 3-365; curve 4-312.

A study of brightness as a function of the temperature at constant excitation (Fig. 7) has shown that temperature quenching occurs at lower temperatures for large crystals than for smaller ones. (In all cases, the ratio of J_{27} , the brightness for large crystals, to $J_{12.5}$, the brightness for small ones, decreases with increasing temperature.) The behavior of the $J_{27}/J_{12.5} = f(T)$ curves varies somewhat for excitation by different wavelengths.

The differences between the optical characteristics of small and large crystals which we have described indicate the existence of certain differences in the properties of their luminescence centers and capture levels. It is possible that crystals of different sizes have slightly different chemical compositions. However, the most probable cause of this behavior probably lies in certain physical effects which arise during phosphor preparation, due to differences in the conditions of crystal growth. The differences indicated are so small, however, that they cannot be revealed by x-ray methods. This makes it impossible to specify their nature.

REFERENCES

1. P. Lenard and V. Klatt, *Ann. Physik* **12**, 439 (1903).
2. N. Riehl and H. Ortman, *Ann. Physik* **29**, 556 (1937).
3. G. R. Fonda, *Phys. Chem.* **43**, 561 (1939).
4. M. S. Oldham and W. Kunert, *J. Opt. Soc. Am.* **31**, 102 (1941).
5. Z. Bodo, *Acta Phys. Acad. Sci. Hung.* **1**, 135 (1952).
6. F. Frey, *Ann. Phys.* **2**, 145 (1948).
7. V. L. Levshin and I. V. Veits, *Zhur. Eksptl. i Teoret. Fiz.* **20**, 411 (1950).

8. J. Broser and W. Reichardt, *Z. Physik* **134**, 222 (1953).
9. F. D. Klement and R. I. Gindina, *Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR. No. 4*, 3 (1956).
10. A. S. Povarennykh, *Trudy Krivorozh. Gorn. Inst. Geol. i Mineral. No. 2* (1958).
11. B. I. Stepanov and Yu. I. Chekalinskaya, *Trudy Inst. Fiz. i Mat. Akad. Nauk Bessarab. SSR, issue no. 2*, 19 (1957).
12. Yu. I. Chekalinskaya, *Trudy Inst. Fiz. i Mat. Akad. Nauk Bessarab. SSR, No. 2*, 38 (1957).
13. N. A. Figurovskii, "Sedimentometricheskii Analiz" (Sedimentometric Analysis). *Izd. Akad. Nauk SSSR, Moscow, Leningrad*, 1948.
14. V. L. Levshin, N. S. Borodin, and G. P. Neronova, *Opt. i Spektr.* **3**, 258 (1957).
15. V. L. Levshin and V. F. Tunitskaya, *Opt. i Spektr.* **8**, 663 (1960), *Optics and Spectroscopy* **8**, 350 (1960).
16. V. V. Antonov-Romanovskii, *Zhur. Eksptl i Teoret. Fiz.* **26**, 459 (1954).
17. E. M. Brumberg and F. M. Pekerman, *Doklady Akad. Nauk SSSR* **13**, 218 (1949).
18. N. A. Vlasenko, *Mater. VII Soveshch. po lyuminestsentsii* (Proc. Seventh Conf. on Luminescence), Tartu, 1959, p. 365.
19. M. N. Alentsev and E. I. Panasyuk, *Opt. i Spektr.* **5**, 207 (1958).
20. N. A. Vlasenko, *Opt. i Spektr.* **7**, 511 (1959), *Optics and Spectroscopy* **7**, 320 (1959).

MEASUREMENT OF THE TRANSMITTANCE OF A LIGHT-SCATTERING MEDIUM AS A METHOD OF STUDYING INHOMOGENEITIES IN IT

A. I. Slutsker and V. A. Marikhin (pp. 512-517)

Received 9 June 1960

Based on the exact Mie theory, equations are obtained relating the transmittance of a scattering medium to the properties of inhomogeneities in it (their dimensions, shape, concentration, and nature). A method and apparatus are described for determining the dimensions and refractive index of inhomogeneities, and a comparison is made between this method and the results of other authors.

When light traverses a medium containing inhomogeneities (particles) with a refractive index different from that of the medium, the light is scattered and the primary beam is thereby attenuated. Together with measurements of the angular distribution of luminance and the degree of polarization of the scattered light, the transmittance of the scattering medium is of great importance; this is the ratio of the luminous flux traversing the medium to that incident on it. A knowledge of this quantity can give much information on the inhomogeneities scattering the light; their dimensions, shape, nature, and concentration may be determined.

Measuring the transmittance of a medium containing inhomogeneities is sometimes simpler and more convenient than obtaining the light-scattering indicatrix, but it is always important to distinguish from the total attenuation that part arising from elastic scattering* of the

*We shall consider elastic scattering to be scattering without change in wavelength.

light flux incident on the inhomogeneities. In the visible region of the spectrum it is possible to study the transmittance of solutions of substances of high molecular weight, colloidal systems, partially crystallized polymers, transparent solids with discontinuities or non-absorbing impurities, fogs, etc.

Several methods have been suggested for reducing the experimental transmittance data for scattering media, based on approximate theories of light scattering in inhomogeneities with properties little different from those of the surrounding medium.^{1,2} However, these approximations may lead to considerable errors in determining the properties of the inhomogeneities (below, we give a more detailed account of the errors arising from the application of approximate theories to the analysis of the

experimental transmittance data). In the present paper we will use the exact Mie theory to obtain equations which allow determination of the dimensions, shape, nature, and concentration of inhomogeneities from a study of the transmittance of a scattering medium.

It is well known that when identical particles are randomly distributed in a medium and when no interference occurs between the waves scattered from individual particles, the attenuation of a light beam passing through the medium is given by Beer's law:

$$I = I_0 e^{-k_p N h}, \quad (1)$$

where I_0 is the luminance of the incident light beam, I is the luminance of the light beam after passage through a thickness h of the medium, N is the concentration of particles, and k_p is the scattering coefficient for a single particle (the total flux of electromagnetic energy scattered by the particle in all directions divided by the incident flux density), with dimensions of area, sometimes called the scattering cross section of the inhomogeneity.

For spherical particles of radius R we can write³:

$$k_p = \pi R^2 K, \quad (2)$$

where πR^2 is the geometrical "shadow" of the inhomogeneity and K is a dimensionless quantity depending on the diffraction behavior of the particle (for particles with dimensions less than the wavelength λ of the incident light, K is less than unity; for inhomogeneities with $R > \lambda$, K exceeds unity).

It follows from the Mie theory that

$$K = K\left(\frac{R}{\lambda_0} m_a, m_i\right),$$

where λ_0 is the wavelength of light in a vacuum, and m_i

and m_a are the refractive indices of the particle and the medium surrounding it, respectively.

Introducing the notation

$$\rho = \frac{2\pi R}{\lambda_0} m_a,$$

we may write

$$K = K(\rho, m_i).$$

From Eqs. (1) and (2) we find:

$$\ln \frac{I}{I_0} = -\pi R^2 K(\rho, m_i) N h$$

or:

$$\ln \left| \ln \frac{I}{I_0} \right| = \ln K(\rho, m_i) + C,$$

where $C = \ln(\pi R^2 N h)$.

Further:

$$\begin{aligned} \frac{d \left\{ \ln \left| \ln \frac{I}{I_0} \right| \right\}}{d(\ln \lambda_0)} &= \frac{d[\ln K(\rho, m_i)]}{d(\ln \lambda_0)} \\ &= \frac{1}{K(\rho, m_i)} \cdot \frac{dK(\rho, m_i)}{d(\ln \lambda_0)} = \frac{1}{K(\rho, m_i)} \lambda_0 \frac{dK(\rho, m_i)}{d\lambda_0}. \end{aligned}$$

We will assume that dispersion is absent or small, that is, that m_1 and m_a are independent of λ_0 in the region of interest (this is valid for the spectral region in which there are no absorption bands of the substances under study).

We then get:

$$\frac{1}{K(\rho, m_i)} \lambda_0 \frac{dK(\rho, m_i)}{d\lambda_0} = \frac{\rho}{K(\rho, m_i)} \cdot \frac{dK(\rho, m_i)}{d\rho}.$$

We introduce the notation:

$$\eta(\rho, m_i) = \frac{d \left\{ \ln \left| \ln \frac{I}{I_0} \right| \right\}}{d(\ln \lambda_0)} = \frac{\rho}{K(\rho, m_i)} \cdot \frac{dK(\rho, m_i)}{d\rho}. \quad (3)$$

We see from Eq. (3) firstly, that $\eta(\rho, m_i)$ can be obtained from an experimental determination of I_0 , I , and λ_0 , and secondly that it can be related to the properties of a single inhomogeneity (its size R and its nature as reflected in the quantity m_i) and evaluated theoretically if the function $K(\rho, m_i)$ is known. $K(\rho, m_i)$ can be evaluated from Mie theory if m_a and m_i are known. As an illustration, Fig. 1 gives the function $K(\rho, m_i)$ for a water drop in air.⁴

Further, the function $\eta = \eta(\rho, m_i)$ can be obtained by numerical or graphical differentiation. Figure 2 shows the function $\eta = \eta(\rho)$ for a water drop in air. It is seen that, starting with the value 4 for $\rho \rightarrow 0$ (Rayleigh scattering), this quantity decreases with increasing ρ , passes

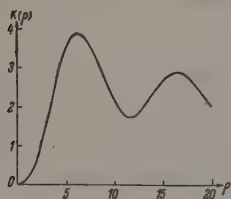


Fig. 1

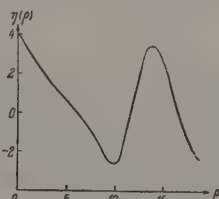


Fig. 2

Fig. 1. The scattering coefficient for a water drop in air ($m = 1.33$).

Fig. 2. The function $\eta = \eta(\rho)$ for a water drop in air. $\eta = \rho/K(\rho) \cdot \partial K(\rho)/\partial \rho$.

through zero at the extremal points of the function $K(\rho, m_i)$, and is oscillatory in nature.

In practice only the initial section of the $\eta = \eta(\rho, m_i)$ curve is needed to determine the properties of the inhomogeneities from light scattering, since, at larger values of ρ the particles become visible with an ordinary microscope.

It is very easy to reduce the experimental data by the method explained above. The fraction (I/I_0) of the light which penetrates the specimen is measured as a function of wavelength λ_0 and then the double logarithm of the transmittance $\ln|\ln(I/I_0)|$ is plotted graphically as a function of the logarithm of the wavelength $\ln \lambda_0$. The slope of the curve obtained near the appropriate value of λ_0 gives the value of $\eta(\rho, m_i)$, from which the quantity ρ is determined from a graph of the type of Fig. 2. To construct the computational graph $\eta(\rho, m_i)$ as indicated above, the value of m_i , that is, the nature of the inhomogeneities, must be known beforehand. After ρ is determined, it is obviously easy to find the radius of the inhomogeneities.

This method may also be applied to determining the refractive index m_i of the particles, that is, their nature, if from other independent measurements (optical or nonoptical) the value of R is known. In fact, if a family of curves of $\eta(\rho, m_i)$ is constructed for different m_i , a graph of the type of Fig. 3 is obtained. If $\eta(\rho, m_i)$ has been determined experimentally and ρ is known, among the family of curves of Fig. 3 one with parameter m_i will be found such that the values of R obtained from it agree best with the experimental ones. In this way the value of m_i for the particles is established, which gives information on their nature.

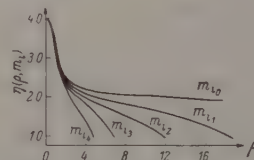


Fig. 3. Curves of $\eta(\rho, m_i) = f(\rho)$ for various m_i . $|m_a - m_{i4}| > |m_a - m_{i3}| > \dots > |m_a - m_{i0}|$.

From Fig. 3 we see that the curves of $\eta(\rho, m_i)$ for the different values of m_i are very close together in the range $\rho < 1.5$ (that is, at $\lambda_0 = 5000 \text{ \AA}$ and $R \lesssim 800 \text{ \AA}$). This prevents us from finding m_i by the above-mentioned method at $R < 800 \text{ \AA}$ but, on the other hand, allows us to estimate the dimensions of the particles independently of their nature, which is frequently very useful.

As we have already mentioned, several authors^{1,2} have suggested reducing experimental data by methods based on approximate theories of light scattering. Thus, in ref. 1, the author starts from the empirical equation⁵:

$$k_p = \text{const } \lambda^{-n}, \quad (4)$$

where k_p is the scattering coefficient and n is a numerical factor depending only on the particle dimensions and independent of the wavelength λ of the incident light.

In this case the slope of experimental straight lines, also plotted in coordinates $\ln|\ln(I/I_0)|$ and $\ln \lambda$, determines a quantity n which has a definite theoretical relationship to the radius of the inhomogeneity (Fig. 5, curve 2). However, describing k_p by Eq. (4) is equivalent to approximating $k_p = f(\rho)$ by a parabola of some degree. Now, as Fig. 4 shows, this approximation is sufficiently accurate to allow calculation of only the absolute values

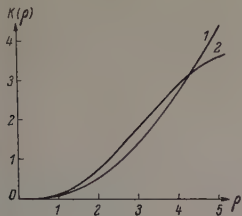


Fig. 4

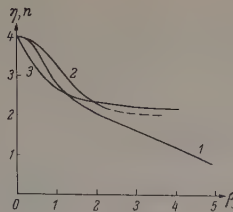


Fig. 5

Fig. 4. Scattering coefficient $K(\rho)$ for $m = 1.33$. Curve 1—according to Shifrin; curve 2—according to Mie theory.

Fig. 5. Theoretical curves $\eta = \eta(\rho)$ and $n = n(\rho)$. Curve 1—according to Mie theory; curve 2—according to Shifrin's theory; curve 3—according to Debye-Bueche theory.

of the scattering coefficients for inhomogeneities but is not accurate enough to give the shape of the function $k_\rho = K(\rho)$ which, according to Eq. (3), also determines the theoretical function $n = f(\rho)$. It follows from Fig. 5, for example, that in the region $\rho \approx 1$ the error in determining the dimensions of the inhomogeneities can reach about 30% and for larger values of ρ this approximation is completely invalid.

Still more significant deviations (especially for low values of ρ) occur in using the function $n = n(\rho)$ obtained in ref. 2 (this theoretical function $n = n(\rho)$ is shown by Fig. 5, curve 3). Thus, for example, at $\rho = 0.5$ the error may reach 100%. Therefore, using approximate theories to analyze experimental data from transmittance measurements, while considerably simplifying the calculations, may lead to considerable errors in determining the properties of the inhomogeneities.

In ref. 6 another method was suggested for determining the dimensions and concentration of inhomogeneities using Mie theory. Starting from Beer's law, the authors obtained the following equations:

$$I = I_0 e^{-k_\rho N h},$$

$$\ln \ln \frac{I_0}{I} = \ln k_\rho + \ln \pi R^2 N h, \quad (5)$$

$$\ln \rho = \ln \frac{1}{\lambda_a} + \ln 2\pi R. \quad (6)$$

If the calculated values of $\ln k_\rho$ are plotted graphically against $\ln \rho$ and also the experimental values of $\ln \ln(I_0/I)$ against $\ln(1/\lambda_a)$, then, in virtue of Eqs. (5) and (6), identical curves should be obtained, displaced relative to each other by $\ln 2\pi R$ along the axis of abscissas and by $\log(\pi R^2 N h)$ along the axis of ordinates. These displacements can be used to obtain the dimensions of the particles and their concentration.

If there are any special features in the curves (for example, extremals), the relative displacements of the curves along the coordinate axes can be determined quite easily, and in this case the method gives a simple way of determining the properties of the inhomogeneities. Practical difficulties arise if the experimental curve $\ln \ln(I_0/I) = f(\ln(1/\lambda_a))$ is a sector of a monotonic curve (this occurs with particles of dimensions up to several hundred Angstroms, that is, in the very important region of submicroscopic inhomogeneities where the use of light scattering to determine the properties of the particles is most desirable). In this case the slopes of the theoretical and experimental curves must be compared, which, in

particular, leads to the method described in the present paper.

The basic feature of the transmittance method as compared with the indicatrix method or the polarization method is that the multiplicity of scattering is unimportant; all that matters is that the beam deviates from its initial direction, and the degree to which this occurs by single scattering is not important. This is very useful in studying objects of relatively high turbidity with which the methods of measuring the indicatrix and the degree of polarization might prove impracticable. With all its advantages, the transmittance method is not free from disadvantages and limitations, among which are the following.

1. The function $\eta(\rho, m_1)$ can be relatively easily calculated and plotted for spherical particles only. For randomly located nonspherical particles the calculations rapidly become complex.^{3,7} However, for oriented nonspherical particles of larger size (up to ~600-700 Å) the calculation becomes easier again, because the quantity $K(\rho, m_1)$ has the same shape as for a sphere (only $\rho = (2\pi H/\lambda_0)m_a$ where H is the size of the particle along the incident light ray—the "ray-parallel dimension").

2. When weakly scattering objects are being studied the method loses its advantage over the others only because of measuring difficulties. In fact, while in the indicatrix method the light scattered is itself measured, small though it may be, in the transmittance method the difference between two large quantities (I and I_0) must be measured; this difference is small for the case of weak scattering and the task is difficult, as it is for any such small-difference measurement.

In conclusion we introduce the experimental arrangement for measuring transmittance. Here two basic conditions must be satisfied simultaneously: the measurement must be repeated in highly monochromatic light at different wavelengths and the rays scattered by the sample must be excluded from the detector.

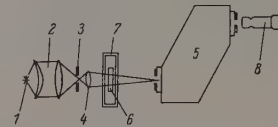


Fig. 6. Diagram of an apparatus for measuring the transmittance of scattering media.

The arrangement of Fig. 6 may be used to satisfy these conditions. A convergent beam of light formed by the source 1, and condenser 2, the slit 3, and the objective 4 passes through the specimen 6 and falls on the entrance slit of the monochromator 5. A photomultiplier 8 placed at the monochromator exit slit can be used as a detector; the specimen should be placed in a plane cell immersed in the liquid 7 to reduce the effect of scattering and reflection from the cell surfaces. In order to meet the second requirement, the slit should be made fairly narrow (which, incidentally, improves the resolution) and the specimen should be placed a fair distance from the slit (so that the amount of scattered light entering the slit will be small).

The measurements are made by the differential method: first the quantity I_0 is measured (with the cell filled with solvent, or when studying turbid solids with a nonturbid equivalent of the specimen placed in the immersion liquid), and then I is measured.

As an example, Fig. 7 shows the results of a series

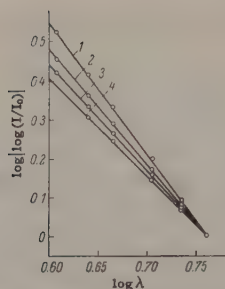


Fig. 7. Experimental variation of $\log|\log(I/I_0)| = f(\ln\lambda)$ for transparent plastic specimens. "Ray-parallel" dimensions H of the particles (in Å): Curve 1—410; curve 2—520; curve 3—650; curve 4—790. The graphs are normalized to one point for all the specimens.

of measurements on transparent plastic specimens inside which were formed submicroscopic bubbles, causing turbidity in the specimens.⁹ The measurements were made with light in the wavelength range 4000 to 6000 Å. The data are plotted in the usual coordinates for the transmittance method. Also shown are the "ray-parallel" dimensions of the bubbles calculated from these data.

The authors are grateful to S. N. Zhurkov for his con-

stant attention and interest in the work and to K. S. Shifrin for valuable advice on light-scattering theory and for his criticism of the results.

REFERENCES

1. I. Ya. Slonim, *Opt. i Spekr.* **8**, 98 (1960), *Optics and Spectroscopy* **8**, 48 (1960).
2. R. S. Keane and I. I. Stein, *J. Polymer Sci.* **20**, 327 (1956).
3. K. S. Shifrin, "Rasseyaniye sveta v mutnoi srede" (Light Scattering in Turbid Media). Gosudarst. Izd. Tekh.-Teoret. Lit. Moscow, Leningrad, 1951.
4. J. A. Stratton and H. G. Houghton, *Phys. Rev.* **38**, 159 (1931).
5. W. Heller and E. Vassy, *J. Chem. Phys.* **14**, 565 (1946).
6. V. K. LaMer, E. C. Y. Inn, and I. B. Wilson, *J. Colloid Sci.* **5**, 471 (1950).
7. F. Möglich, *Ann. Physik* **83**, 609 (1927).
8. S. N. Zhurkov, A. I. Slutsker, and V. A. Marikhin, *Fiz. Tverd. Tela* **1**, 1752 (1959), *Soviet Phys.-Solid State* **1**, 1601 (1960).
9. S. N. Zhurkov, V. A. Marikhin, and A. I. Slutsker, *Fiz. Tverd. Tela* **1**, 1159 (1959), *Soviet Phys.-Solid State* **1**, 1060 (1960).

INCREASE OF PRECISION IN ISOTOPIC SPECTRAL ANALYSIS

M. S. Kashtan and T. N. Khlopina (pp. 518-523)

Received 23 May 1960

A method is developed for the interpretation of the recorder traces which, by a rigorous consideration of the overlapping of the apparent (instrumental) contours of the hyperfine structure (hfs) components, and by elimination of the parasitical continuous background gives a high precision determination of isotope concentration by the spectral method. A rational procedure is suggested for the determination of the isotope concentration in analysis of micro-quantities of lead.

Papers were recently published^{1,2} on the isotopic spectral analysis of lead in which the precision achieved in the determination of small isotope concentrations was insufficient for the solution of a number of problems.

One of the reasons for the insufficient precision is the fact that in the suggested methods of interpretations of the recorder traces either the number of unknowns (including the parasitical background) exceeds the number of equations formed, or (when the parasitical background is excluded) the intensity is used which is distorted by the mutual superposition of components and by the presence of the parasitical background,* instead of

a better method for the interpretation of the recorder traces.

The problem of determination of the true intensity ratios of the hfs components of an analytical line is a special case of the general problem of reducing the apparent spectrum to a true one (see, for instance, the review by Rautian³), and it is called the "incomplete" reduction. The application of the method of "incomplete" reduction is described below for the determination of the ratio of the true intensities of the hfs components (and, consequently, of the isotope concentrations) in the isotopic spectral analysis.

The method consists essentially in the following. Let us assume that the hfs of interest to us consists of n components, the true intensities I_k ($k = 1, 2, \dots, n$) of which must be determined. Moreover, the intensity $i_b(\lambda)$ of the parasitical continuous background present in the recorder traces is also unknown. We assume that the dependence of $i_b(\lambda)$ on the wavelength within the spectral region under study is known and expressed by

$$i_b(\lambda) = \beta(\lambda) I_b, \quad (1)$$

where I_b is the maximum intensity of the parasitical

*The appearance of the parasitical background in the recorder traces might be caused by the presence in the used spectral range of the molecular and continuous spectra of the discharge tube, and by the superposition of the wings of the neighbor lines, as well as by light scattered in different parts of the optical system.

the true component intensities.

The purpose of the present work was to study the possibility of an increase of precision and of concentration sensitivity of isotopic spectral analysis, by using

background within this spectral region. It is apparent that $\beta(\lambda) = 1$, when the parasitical background can be considered constant within this region. Although the determination of the parasitical background is of no practical importance, the introduction of I_b is necessary for obtaining of a complete system of equations. Thus there are $n + 1$ unknowns altogether. For their determination one can write the following system of $n + 1$ equations of the first order:

$$\left. \begin{aligned} \alpha_{11}I_1 + \alpha_{12}I_2 + \dots + \alpha_{1n}I_n + \beta_1I_b &= A_1, \\ \alpha_{21}I_1 + \alpha_{22}I_2 + \dots + \alpha_{2n}I_n + \beta_2I_b &= A_2, \\ \dots &\dots \\ \alpha_{n+1,1}I_1 + \alpha_{n+1,2}I_2 + \dots + \alpha_{n+1,n}I_n + \beta_{n+1}I_b &= A_{n+1}. \end{aligned} \right\} \quad (2)$$

The free terms of the reduced system (2) are the constants A_1 ($l = 1, 2, \dots, n + 1$) which are measured by means of the recorder traces of the hfs in different points of the interference order. The position of at least one of these points in the hfs of the analytical line must be known to serve as a reference point. The coefficients α_{1k} account for the contribution of the true intensities I_k at the points where the values A_1 are measured. It is apparent that the coefficients α_{1k} are determined both by the positions of the hfs components, and by the apparent contour of the lines. These contours depend in general upon the parameters of the apparatus (the contrast of the spectral apparatus, the inertia of the recorder, etc.), as well as upon the excitation conditions of the analytical line in the light source (Doppler broadening, self-absorption, and so forth). It should be also mentioned that the points for measuring the values of A_1 must be judiciously selected, in the sense that the coefficients α_{1k} , for which $l = k$, if possible, must be of the same order of magnitude, and must considerably exceed all other coefficients of the corresponding equation.

Solving the system (2) by the usual method,⁴ we obtain an expression for the determination of the unknowns in the following form

$$\left. \begin{aligned} I_k &= f_k(\alpha_{1k}, \beta_1, A_1), \\ I_b &= f_b(\alpha_{1k}, \beta_1, A_1). \end{aligned} \right\} \quad (3)$$

It is clear that the precision of the determination of intensity I_k of the hfs components depends upon the precision of the determination of the values of α_{1k} , β_1 , and A_1 . When an isotope has several hfs components, the intensities of which are connected by certain ratios (as, for instance, in Pb), the order of the system (2) can be lowered correspondingly, as can be easily seen. This is true also for the case when the element being determined consists of several isotopes, where the concentration ratio of some of them remains constant (as, for instance, in natural Sr).

For the transition from the intensity of the hfs components to the concentration C_i of any of the m isotopes of the element being determined, one can use the formula

$$C_i = \frac{I_i}{\sum_{i=1}^m I_i} \cdot 100 (\%). \quad (4)$$

It must be mentioned that the application of the above method of "incomplete" reduction, as well as of the method of reduction of the apparent spectrum to the true one in general, has natural limits connected with the necessity of taking the disturbances into consideration.⁵

We have used the described method of interpretation of the recorder traces for determination of the isotope

composition of a microquantity of lead (of the order 5×10^{-5} gm).

The experimental work was conducted with a spectrometer equipped with a photoelectric recording in which the apparatus of a high resolving power was a Fabry-Perot interferometer. The analytical line was Pb I 4057.8 Å, the hfs of which consists of six components (Fig. 1 a) belonging to four lead isotopes Pb^{204} , Pb^{206} , Pb^{207} , and Pb^{208} . Three of these components (207a, 207b, and 207c with the intensity ratios 9:5:1) belong to the even-odd isotope Pb^{207} ; according to the above considerations it is possible to reduce the system to five equations for the concentration of the isotopes. The precision of determination of the true intensities of the hfs components (and therefore also of the concentration of the isotopes) depends on the precision of determination of the etalon constant, on the apparent contour of the analytical line, on the distance between the hfs components, the characteristics of the parasitical background, and also on a judicious selection of the points for the experimental determination of the values of A_1 .

We have chosen an etalon Fabry-Perot with a distance between the mirrors equal to 10.00 ± 0.01 mm, at which distance there was no superposition of the hfs components of the adjacent orders of the interference pattern (Fig. 1b). The parameters of the etalon used, the coefficient of reflection of which was 88 per cent, gave a resolution of the components 204, 206, 207b, and 207c such that one could, without an appreciable error, consider them coinciding with the corresponding maxima of the recorder traces of the hfs. This permitted the use of the intensity of these maxima as the experimental values A_{204} , A_{206} , A_{207b} , and A_{207c} which enter into Eq. (1), for determination of the true intensity of the components. Since the components 208 and 207a, with a distance of 0.01 cm^{-1} between them, are not resolved on the recorder traces, the last of the experimental values A_{208} entering the equations was determined at a point which corresponded to the position of the component 208. In order to find this point, and for making all the necessary calculations, the data on hfs of the line Pb I 4057.8 Å obtained by Steudel⁶ were used (Fig. 1a).

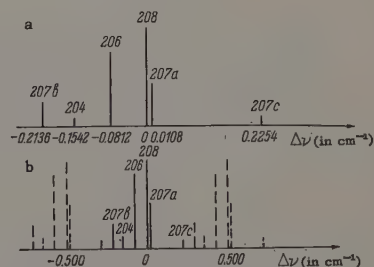


Fig. 1. Hyperfine structure of the line Pb I 4057.8 Å. a—The true distribution; b—the pattern obtained with a Fabry-Perot etalon of 10 mm thickness.

The excitation conditions of the analytical line in the discharge tube were selected in such a way that the self-absorption of the strong components was practically absent. Therefore, when the conditions for the recording were chosen judiciously, the apparent contour was given practically only by the contrast of the interferometer and by the Doppler broadening of the analytical line in the light source.

The calculations performed have shown that for the Doppler contour of the analytical line, excited with weak currents in the discharge tube with a hollow cathode cooled with liquid nitrogen, the intensity at a point in a distance 0.06 cm^{-1} from the maximum is only 8×10^{-5} that of the intensity of the maximum. Therefore the coefficients α_{1k} which account for the superposition of the hfs components, the distance between which exceeds 0.06 cm^{-1} , were calculated according to the Airy formula, which describes the intensity distribution in the interference pattern produced by the Fabry-Perot etalon. The only exceptions are the coefficients which account for the mutual superposition of the components 208 and 207a. The values of these coefficients depend both on the contrast of the interferometer and on Doppler broadening of the components. For determination of these coefficients, the apparent contour under the same working conditions was studied of the component 208 of the hfs line Pb I 4057.8 Å of a lead sample which contained about 97 percent of the isotope Pb^{208} . The experiment has shown that the reflection coefficient of the etalon was actually 87.7 percent.

The numerical values of the coefficients α_{1k} which account for the mutual superposition of the hfs components of the line Pb I 4057.8 Å for the Fabry-Perot etalon used by us are given in Table 1.

Since the spectral region used was very narrow (about 0.07 Å), the parasitical background can be considered as practically constant within these limits; that is, one can assume the coefficients $\beta_1(\lambda)$ equal to unity.

$$\left. \begin{aligned} I_{204} &= 1.0107A_{204} - 0.0180A_{206} + 0.2504A_{207b} - 1.2416A_{207c} - 0.0013A_{208}, \\ I_{206} &= 1.0119A_{206} + 0.2820A_{207b} - 1.2604A_{207c} - 0.0129A_{208} - 0.0201A_{204}, \\ I_{207} &= 3.8700A_{207b} - 3.7712A_{207c} - 0.0001A_{208} - 0.0892A_{204} - 0.0090A_{206}, \\ I_{208} &= 1.0120A_{208} + 0.0379A_{204} - 0.0090A_{206} - 1.5210A_{207b} + 0.4807A_{207c}. \end{aligned} \right\} \quad (6)$$

The experimental factor which determines the precision of the analysis is the reproducibility of the relative intensities of the hfs components in the successive orders of the interference pattern obtained in the recorder traces.

The application of the method described by us earlier, of introducing microquantities of the sample into the hollow cathode as metallic lead,⁷ results in a stabilization of the emission of the analytical line. The reproducibility of the relative intensities of the hfs components in the successive orders of the recorder traces is determined here essentially by the fluctuations of the photocurrent due to the shot effect in the photomultiplier. It is clear that the fluctuations affect more seriously the reproducibility of the relative intensity of the weak hfs components (to which the component 204 belongs). In order to reduce the influence of the shot effect on the repeatability of the relative intensity of weak components, it is necessary to amplify considerably the signals coming from them to the photomultiplier. This can be achieved by various means: firstly, by an increase of the speed of the optical arrangement; secondly, by enhancing the intensity of the emission of the analytical line by an increase of the discharge current, and thirdly, by recording the strong and the weak hfs components at different discharge currents. It is apparent that the first method is best; however, at present we had no means to realize it. The second method involves the necessity of taking into consideration the influence of the self-absorption on the apparent contour of the strong components, which leads to additional errors.

Table 1

Components	204	206	207a	207b	207c	208
204	1.0000	0.0215	0.0055	0.0314	0.0086	0.0060
206	0.0215	1.0000	0.0135	0.0074	0.0046	0.0178
207a	0.0055	0.0135	1.0000	0.0042	0.0043	0.7800
207b	0.0314	0.0074	0.0042	1.0000	0.0298	0.0043
207c	0.0086	0.0046	0.0043	0.0298	1.0000	0.0042
208	0.0060	0.0178	0.7800	0.0043	0.0042	1.0000

This assumption is confirmed by the experimental study of the recorder traces in the spectral region in question which were obtained at the same working conditions in the discharge tube, but without introducing the lead sample.

By using the coefficients α_{1k} given in Table 1 and the ratios of the true intensities of the components 207a, 207b, and 207c, and by considering that $I_{207} = I_{207a} + I_{207b} + I_{207c}$ and that $\beta_1(\lambda) = 1$, it is not difficult to bring the system of equations (2) for the case in question to the form

$$\left. \begin{aligned} I_{204} + 0.0215I_{206} + 0.0144I_{207} + 0.0060I_{208} + I_b &= A_{204}, \\ 0.0215I_{204} + I_{206} + 0.0109I_{207} + 0.0176I_{208} + I_b &= A_{206}, \\ 0.0086I_{204} + 0.0046I_{206} + 0.0791I_{207} + 0.0042I_{208} + I_b &= A_{207a}, \\ 0.0315I_{204} + 0.0074I_{206} + 0.3377I_{207} + 0.0043I_{208} + I_b &= A_{207b}, \\ 0.0060I_{204} + 0.0176I_{206} + 0.4469I_{207} + I_{208} + I_b &= A_{208}. \end{aligned} \right\} \quad (5)$$

The solution of the system (5) gives the true intensities of the components I_{204} , I_{206} , I_{207} , and I_{208} expressed through the experimentally determined values of A_{204} , A_{206} , A_{207b} , A_{207c} , and A_{208} :

Therefore the last method was used, although the measurements had to be made in two steps. After recording five or six orders of the interference pattern with a discharge current of 1.5–1.6 ma, at which current the distortion of the contour of the strong components due to self-absorption is not yet noticeable (Fig. 2a), the discharge current is increased to 2.2–2.6 ma, and the weak components are recorded in the five or six successive orders (Fig. 2b). The repeatability of the relative intensity of the hfs components thus obtained is given in Table 2 as the average values, and the mean square errors of the intensity ratios of the individual components to the total intensity of the components of the respective interference orders.

The precision of determination of the isotope composition of microquantities of lead by using the described

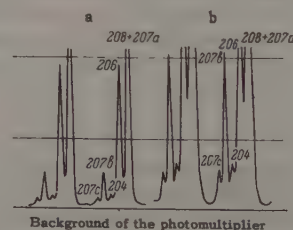


Fig. 2. Recorder traces of the hyperfine structure of the line Pb I 4057.8 Å at the discharge current values 1.5 ma (a) and 2.6 ma (b).

Table 2

No.	$\frac{A_{\text{sp1+sp2}}}{\Sigma A_s}$	$\frac{A_{\text{sp1}}}{\Sigma A_s}$	$\frac{A_{\text{sp2}}}{\Sigma A_s}$	$\frac{A_{\text{sp3}}}{\Sigma A_s}$	$\frac{A_{\text{sp4}}}{\Sigma A_s}$
1	0.6102 ± 0.0014	0.2630 ± 0.0011	0.0776 ± 0.0004	0.0222 ± 0.0003	0.0269 ± 0.0003
2	0.8441 ± 0.0020	0.1153 ± 0.0008	0.0208 ± 0.0006	0.0087 ± 0.0004	0.0111 ± 0.0004

procedure of recording of hfs, and of the described method of interpretation of the recorder traces is demonstrated by the data in Table 3, where, for comparison, the results of the mass-spectrometric analysis are given.

It can be seen from these data that even in the case when the parasitical background is present, and the apparent contours of the hfs components are superimposed, the precision of determination of the isotope concentration by the spectral method using the method of "incomplete" reduction is approaching the precision of mass-spectrometric analysis. This is particularly important when microquantities of material are analyzed, because a further increase of contrast in the Fabry-Perot etalon is accompanied by a considerable decrease of the speed of the spectrometer. On the other hand, an increase of the discharge current makes it necessary to take into consideration the self-absorption, and also results in a sharp decline of the intensity of the analytical line since the microquantities of the sample being analyzed burn out fast, and this, of course, lowers the precision of the analysis.

The writers express their gratitude to L. A. Khalfin for a discussion of the results of this work.

Table 3

No.	Method used	Isotope concentration (%)			
		Pb ²⁰⁸	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²¹⁰
1	Spectral analysis	52.48	25.25	20.86	1.40
		51.88	25.62	21.12	1.37
		51.62	25.51	21.50	1.36
2	Mass-spectrometric analysis	52.18	25.20	21.25	1.37
		52.06	25.24	21.33	1.37
		84.82	10.28	4.68	0.23
2	Mass-spectrometric analysis	85.94	9.57	4.23	0.26

REFERENCES

1. I. K. Brody, F. S. Tomkins, and M. Fred, *Spectrochim. Acta*, **8**, 329 (1957).
2. A. N. Zaidel, A. G. Zhiglinskii, and Yu. Chaiko, *Czechoslov. J. Phys.* **8**, 530, 665 (1958).
3. S. G. Rautian, *Uspekhi Fiz. Nauk* **66**, 475 (1958), *Soviet Phys.-Uspekhi* **1**, 245 (1959).
4. V. I. Smirnov, "Kurs vysshei matematiki" (A Course of Higher Mathematics), Vol. 3, p. 1. Gosudarst. Izd. Tekh. i Teoret. Lit., Moscow, Leningrad, 1949.
5. L. A. Khalfin, *Trudy IV Vsesoyuz. Soveshchaniya Teori Veroyatnosti i Matematicheskoi Statistike* (Trans. IV All-Union Conf. on the Probability Theory and Mathematical Statistics), Erivan, 1959.
6. A. Steudel, *Z. Physik*, **133**, 438 (1952).
7. M. S. Kashtan, E. V. Sobotovitch, and T. N. Khlopina, *Opt. i Spektr.* **8**, 23 (1960), *Optics and Spectroscopy* **8**, 11 (1960).

ON A POSSIBLE CAUSE OF THE "CARRIER" EFFECT IN SPECTRAL ANALYSIS

Ya. D. Raikhbaum and V. D. Malykh (pp. 524-527)

Received 26 May 1960

The mean time τ the impurity atoms remain in the excitation zone of an arc discharge was determined spectroscopically. It is demonstrated that the introduction of the "carrier" into the boring of the arc electrodes results in an increase of this time by two- or threefold. The action of the "carrier" depends on the ionization potential of the impurity atoms, and is connected with the distribution of the electric field in the arc column. Measurements with probes show that in the presence of the "carrier" the radial gradient of the field in the arc column is decreased, and this must result in the decrease of the rate of diffusion of the positive ions into the surrounding atmosphere and to a corresponding increase of τ for the atoms of the element. The effect may be caused by an increased concentration of the negative ions in the discharge plasma when the vapors of the "carrier" enter the latter.

It is known that an addition of small amounts of certain compounds ("carriers") to the material being analyzed results in an increase in the intensity of lines of the elements being determined, and to a corresponding increase of the sensitivity of detection. The study of the "carrier" effect¹⁻³ has shown that it is not connected directly with a change of excitation conditions for the admixture atoms, but is caused by the influence of the "carrier" on the distribution of these atoms in the discharge gap, and by the processes of their passage through the discharge into the surrounding atmosphere. According to the assumption of Zaidel, et al.,¹ the increase in the intensity of impurity lines is explained by the increase in the time the atoms remain in the discharge due to the decrease of the diffusion rate and to convection transfer.

In order to test this assumption, we used a spectrographic method of determination of the mean time the atoms remain in the excitation zone of the discharge.

The compounds used as "carriers" were placed in the boring of the electrodes of a dc arc. The electrodes were prepared from spectroscopically pure carbons, with a boring of 3 mm diameter, 3 to 5 mm long, and with a wall thickness of 0.5 to 1 mm. The experiments were conducted with an arc of 5 to 15 amp, whereby the lower electrode was the anode.

The admixture elements used for the study of the "carrier" effect were applied in the form of sufficiently volatile compounds on the surface of the probe. The latter were made of nichrome wire of 0.2 mm diameter, 80 to 100 mm long, and were fastened to the axis of a

synchronous motor SD-60 fed by a generator ZG-12. During the rotation of the motor, the probes crossed the arc column in the middle of the discharge gap moving in a horizontal plane. The linear velocity of the probe motion in the discharge gap could be varied between 30 and 120 cm/sec. The vaporization of the elements and the passage of the vapors into the discharge was of short duration and took place during the crossing of the arc by the probe.

The spectrograph KS-55 with glass optics and a two-channel photoelectric attachment was used for recording the element lines. The changes in the intensities of two lines and the current of the probe, which was connected through the oscillator of the oscillograph and a resistor with the cathode electrode of the arc, were measured simultaneously.

After the emerging of the probe from the arc (which was indicated by the oscillograms of the probe current), when the supply of vapors of the element from the probe surface into the arc has ceased, the intensity of the lines decreased exponentially (Fig. 1). Evaluation of the oscillograms permitted the determination of the mean time τ the atoms remain in the excitation zone.

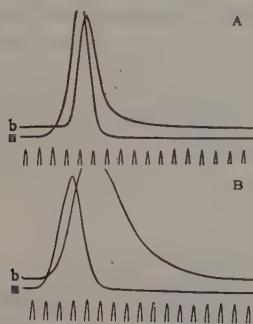


Fig. 1. Oscillograms of the probe current (curve a) and of the intensity of the spectral line Tl 5350.46 Å (curve b) in a carbon arc (A) and after the introduction of AgCl into the arc (B). Time marks—0.002 sec.

The introduction into the boring of the electrode of a carbon arc of various compounds leads to changes in the value of τ . Some increase of τ was observed in most cases which could be explained by the lowering of the arc temperature resulting in a reduction of the rate of diffusion of atoms. Only in cases when lines of a high excitation energy were used for measurements was a decrease of τ was observed, apparently caused by the decrease of the radius of the excitation zone following the drop of the arc temperature.

Characteristic changes of τ took place also when compounds were placed into the electrode boring, which are used as "carriers" (gallium oxide, halide compounds). As follows from the data given in Tables 1 and 2, the value of τ for atoms with low ionization potential increased substantially in this case. This effect diminished with the increase of the ionization potential and disappeared completely for mercury ($V_i = 10.43$ ev). Accordingly, changes in intensity of the impurity lines, characteristic of the "carrier" effect, must take place. The dependence of the "carrier" effect on the ionization potential of admixtures was pointed out earlier by Vukovich.⁴

The influence of the halide compounds on the mean time the admixture atoms remain in the excitation zone

Table 1. Change of the Mean Time During Which the Atoms of Lithium and Thallium Remain in the Excitation Zone in the Presence of a "Carrier" (Carbon dc arc ~ 10 amp)

Element	Line wavelength (Å)	$\tau \times 10^3$ (sec)			
		Without "carrier"	Metal silver	Silver chloride	Gallium oxide
Lithium	4602.86	1.0	1.1	2.4	1.95
Thallium	5350.46	1.9	2.1	4.6	3.8

is connected with the electron affinity of the halide atoms. The largest increase of τ was observed invariably when fluorine compounds were introduced into the arc (the electron affinity for fluorine atoms is 4.13 ev). The increase in the value of τ was smaller when chlorine, bromine, and iodine compounds were introduced into the arc (Table 3). The electron affinity for atoms of chlorine, bromine, and iodine is 3.75, 3.54, and 3.14 ev, respectively.⁵

Table 2. Dependence of the "Carrier" Effect on Ionization Potential of Admixture Atoms (Carbon dc arc ~ 15 amp)

Element	Ionization potential (ev)	Line wavelength (Å)	Excitation potential of the line (ev)	$\tau \times 10^3$ (sec)		Relative change of τ
				Without "carrier"	Gallium oxide	
Lithium	5.39	4602.86	4.54	1.4	2.6	1.88
Thallium	6.11	5350.46	3.28	3.0	5.2	1.73
Zinc	9.39	4810.53	6.66	2.7	4.3	1.59
Mercury	10.43	4358.35	7.73	6.0	5.3	0.88

The results of the measurements permitted the conclusion that the "carrier" effect is connected with the increase of time the admixture atoms remain in the excitation zone of the discharge, as it was assumed before. However this increase of τ is caused not only by the changes of the thermal, but also of the electrical parameters in the arc column. In connection with this question, we have performed probe measurements of the radial field distribution in the arc column.

Table 3. Change of τ for Atoms upon Introduction of Various Chemical Compounds into the Arc (Carbon dc arc ~ 10 amp)

Element	Line wavelength (Å)	Without additions	$\tau \times 10^3$ (sec)							
			Li ₂ CO ₃	LiF	LiCl	LiJ	Na ₂ CO ₃	NaF	NaCl	NaBr
Lithium	4602.86	1	—	—	—	—	2.3	3.5	2.3	3.0
Thallium	5350.46	1.95	3.7	6.0	4.2	2.7	3.7	6.7	3.7	4.5
Mercury	4358.35	3.8	2.7	2.9	2.7	—	2.6	2.8	2.9	2.5

Double rotating probes were used in these measurements consisting of two insulated nichrome wires 0.2 mm in diameter, spaced 1.5 mm apart. Both wires crossed the arc simultaneously in the middle of the discharge gap, moving in a horizontal plane with a velocity 80 cm/sec. A current resulted in the probe circuit (Fig. 2) which was determined by the potential difference in the two wires which were at different distances from the arc axis. The current was recorded with an electronic oscillograph EO-7. The probe method of investigation of an electric arc involves some difficulties which are caused by the disturbance of the arc by the probe, and by the fact that it is not possible to estimate with sufficient accuracy the potential difference between the probe and the plasma.^{6,7} Nevertheless, by means of the probes valuable information can be obtained concerning the relative distribution of the potential in the arc column.⁸ Therefore the oscillograms

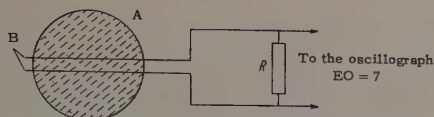


Fig. 2. Schematic diagram of the field measurement with a double probe. A—horizontal cross section of the arc column; B—double probe; R—resistance (100 kohm).

of the current obtained by us in the double probe give some conception of the characteristics of the radial distribution of the electric field in the arc column. The application of wires instead of point probes cannot change the characteristics of the oscillogram substantially, because the potential of the probe is given mainly by the potential of that spot in the plasma in touch with the probe, which corresponds to the highest conductivity.⁸

The oscillograms of the current from the double probe (Fig. 3) were symmetric with respect to the arc axis; the direction change of the current was caused by the variable polarity of the wires. The shapes of the oscillograms were often distorted because of the displacements of the arc, and because of the convection air current.

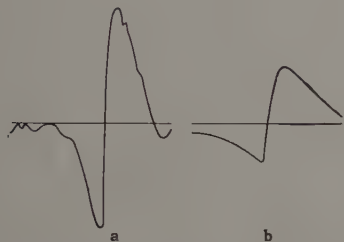


Fig. 3. Oscillogram of the current from the double probe for a carbon arc (a) and for an arc with addition of AgCl (b).

The measurements with probes have demonstrated that the introduction of the "carriers" into the arc results in a substantial decrease of the field gradient in the radial direction of the column. Figure 4 gives results of calculations of the horizontal gradient of the electric field in the arc column, made on the basis of probe measurements for cases when various compounds were introduced into the electrode boring. These changes of the field must result in a decrease in the rate of diffusion of the positive atoms, in a diminishing of their losses in the arc column, and in an increase in the mean time the atoms are in the arc. The influence of the "carrier" will

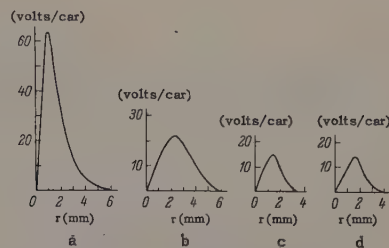


Fig. 4. Distribution of the electric field gradient in the arc column in the radial direction upon introduction of various compounds into the arc. a—carbon arc; b—same with Li_2CO_3 ; c— LiF_2 ; d— Ga_2O_3 .

be apparent to a larger degree, when the ionization potential is lower and the concentration of its ions is higher.

The reason for the observed weakening of the field in the radial direction may be the formation of negative ions. As calculations show, the probability of this process (particularly in the peripheral parts of the discharge) is greatest for atoms of oxygen and halogens which form a part of the molecules of the "carriers." The increase of concentration of the negative ions is accompanied by an equalizing of the mobilities of the positively and negatively charged particles in the plasma, by a decrease of the density of the space charges, and leads to more uniform field distribution in the arc gap. The change in the shape of the cloud in the arc gap observed by Vainshtein and Belyaev,² upon the introduction of the "carrier" into the arc, may be connected with the above conditions.

REFERENCES

1. A. N. Zaidel', N. I. Kaliteevskii, G. G. Kund, and Z. G. Fratkin, *Opt. i Spekr.* **2**, 29 (1957).
2. E. V. Vainshtein and Yu. I. Belyaev, *Zhur. Anal. Khim.* **13**, 388 (1958).
3. Yu. I. Belyaev, E. V. Vainshtein, and V. V. Korolev, *Zhur. Anal. Khim.* **14**, 147 (1958).
4. V. M. Vukanovic', *Rev. universelle mines* **15**, 390 (1959).
5. V. L. Granovskii, "Elektricheskii tok v gazakh" (Electric Current in Gases), Vol. 1. Gosudarst. Izd. Tekh. i Teoret. Lit., Moscow, Leningrad, 1952.
6. G. Müller, *Z. Physik* **151**, 460 (1958).
7. C. Fragstein and M. Arndt, *Ann. Physik* **33**, 535 (1938).
8. G. Müller and W. Finkelburg, *Z. angew. Phys.* **8**, 282 (1956).

AN INTEGRATING SPHERE ATTACHMENT TO THE SF-4 SPECTROPHOTOMETER FOR MEASUREMENT OF DIFFUSE REFLECTION AND TRANSMISSION COEFFICIENTS

A. S. Toporets (pp. 528-532)

Received 13 June 1960

The construction of an integrating sphere device which makes possible the measurements of absolute values of diffuse reflection and transmission coefficients in a wide spectral region is described. Measurements of the reflection coefficients of a series of powdered objects in the interval from 245 to 700 millimicrons are presented.

Previously we developed an attachment to the SF-4 spectrometer for the measurement of diffuse reflection coefficients.¹ The principal part of this device is an elliptic mirror with the sample placed in one focal plane and a detector in the other. With this equipment it is possible to measure relative reflection coefficients in the spectral region from 250 mμ.

In the present paper an integrating sphere device permitting measurement of absolute values of reflection coefficients in a wide spectral region including the ultraviolet, proposed by Taylor,² will be described.

A basic feature of photometric measurements with an integrating sphere is that one must record light fluxes which have been considerably attenuated.

It is easy to show this by a simple calculation. Let a light flux Φ enter the sphere. Being scattered in the sphere, this flux makes an illumination on the walls equal to

$$E = \frac{\Phi}{4\pi R^2} \cdot \frac{\rho}{1-\rho}, \quad (1)$$

where R is the radius of the sphere and ρ is the reflection coefficient of the walls of the sphere. Flux falls on the detector equal to

$$\Phi_1 = Es = E\pi r^2,$$

where r is the radius of the detector's receiving surface. Substituting the value of E from (1) we have

$$\Phi_1 = \frac{\Phi}{4} \cdot \frac{r^2}{R^2} \cdot \frac{\rho}{1-\rho}. \quad (2)$$

We will assume $R = 60$ mm, $r = 10$ mm, and $\rho = 0.5$ (ultraviolet region). Then between the measured and incident fluxes the relationship

$$\Phi_1 = 0.007 \Phi,$$

is found, i.e., the measured flux consists of less than one percent of the incident flux. Consequently, in measurements with a spherical attachment it is necessary to use either a more powerful light source or a more sensitive detector.

It is well known that extrahigh pressure mercury and fluorescent lamps are some tens of times brighter in the ultraviolet region than the low power hydrogen lamp used in the SF-4 spectrophotometer. However, their use for spectrophotometric purposes introduces a series of difficulties. First and foremost there arises the necessity of using complex arrangements for the stabilization of the higher-power discharge current (greater than 1 amp). Besides that, the luminous wire of these lamps will not remain steady and the oscillations of brightness from the motion of the image of the wire on the entrance slit of the

monochromator can reach tens of percent. The use of a high power hydrogen lamp likewise does not solve the problem, since the brightness of such lamps is only a few times greater than the brightness of the low power hydrogen lamp. Thus there remains the second possibility of using a more sensitive detector.

For some years past photomultipliers have been used as detectors in spectrophotometers, making it possible to record significantly weaker light fluxes than by using an arrangement with photocells. In our arrangement a photomultiplier is also used, incorporated into the SF-4 spectrophotometer circuit by a method described in the literature.³ We used a FEU-25 photomultiplier with a semitransparent photocathode deposited on the inner surface of the flat window. The choice of this type of photomultiplier permits one to place the photocathode near enough to the aperture in the sphere. However, since the photomultiplier window is of ordinary glass, it is insensitive to radiation of wavelengths shorter than 300 mμ. Therefore, we used a luminescent screen of ZhS-9 glass. This screen was not a flat plate, but rather a layer of powder of particle size 0.5-0.7 mm. The photomultiplier window was coated with an aqueous solution of gelatin onto which the powdered glass was dusted. After the gelatin dried the powder layer was securely held on the surface of the window.

The spectral characteristics of the powder screen

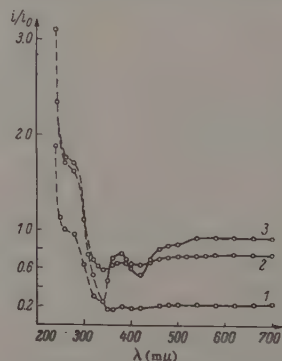


Fig. 1. Spectral characteristics of the luminescent powder screen (curves 1, 2) and the flat plate (curve 3). In the $\lambda > 350$ mμ region the curves represent reflection (curve 1) and transmission spectra (curves 2, 3); the broken parts of the curves determine the course of the sum of two magnitudes—the coefficient of transmission (reflection) and the ratio of the signal produced by the luminescent light to the comparison signal.

and a flat plate of ZhS-9 glass are presented in Fig. 1. Curves 1 and 2 characterize respectively the reflection and transmission spectra of the powder screen in the $\lambda > 350 \text{ m}\mu$ region and curve 3 the transmission spectrum of the flat plate in the same spectral region. Under the action of radiation of wavelength shorter than $350 \text{ m}\mu$ ZhS-9 glass luminesces, as a result of which the light flux registered by the photomultiplier in this spectral region consists of two parts—light passing through the screen (or reflected from it) and luminescent light. Consequently in this case the curves no longer characterize the transmission (or reflection) spectrum but the relative value of the signal generated by light from the source and the luminescent light. In the $\lambda < 290 \text{ m}\mu$ spectral region, it is evident that only luminescent light falls on the photocathode.

From a comparison of curves 2 and 3 it is seen that the effectiveness of the powder screen is 1.5–2 times higher than that of the flat plate. The more intense luminescence of the powder screen is explained by light scattering which increases the coefficient of utilization of the exciting light.

The construction of the attachment with the integrating sphere is shown in Fig. 2. The heavy metal block 1 is fastened by three bolts to the SF-4 spectrophotometer. The photometric attachment is held on the block by grooved guides. A light beam from the exit slit of the monochromator passes through the aperture 2 and, being reflected from mirror 3 through aperture 6, enters into the sphere. Here it falls either on the wall of the sphere or on the sample 11, inserted in aperture 7 in the carriage 10. Light scattered inside the sphere makes some illumination on the walls. The level of this illumination is measured by photomultiplier 12 located at the aperture 8 in the housing 13. Aperture 8 is covered by the shutter 15 which is mechanically connected with a switch such that on opening the shutter the load resistance is disconnected from the ground and is connected to the sensitivity potentiometer.

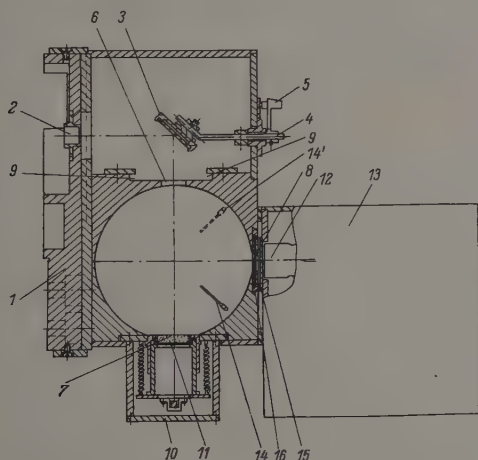


Fig. 2. Construction of the integrating sphere attachment.

Mirror 3 is fastened to shaft 4 which can be turned through a small angle by handle 5. When handle 5 is in the plane of the figure the light beam is directed by the mirror onto the sample. With rotation of the handle to the right or left the beam is directed onto the wall of the sphere. A sample holder containing a sample for meas-

uring the transmission coefficient can be set in grooves 9.

In the lower part of the sphere there are also grooves which hold in place the carriage 10 with a sample for measurement of the reflection coefficient.

There is also a movable screen 14 inside the sphere. Its purpose is to protect the detector from directly incident rays scattered by the sample. For measurement of the transmission coefficient the screen is placed in the upper position and for measuring the reflection coefficient it is placed in the lower position. The transfer of the screen from one location to the other is accomplished with a handle on the front of the device.

The upper carriage is a metallic plate of 5 mm thickness with round holes of 30 mm diameter. The sample to be measured is placed in one of these holes; the other remains open. The carriage can occupy two positions in each of which one or the other hole of the carriage is located opposite the opening 6.

The construction of the lower carriage (body 1, pins 8) is shown in Fig. 3. The cradle for samples is made in the form of cylinders 3 affixed to plate 4 which with springs (Fig. 2) is held up against the upper cover of the carriage. Attached to the plate is a bracket 5 against which the end of lever 6 rests. On pressing a pin on the right end of the lever the plate with the cylindrical cradles is lowered, whereupon the cylinders 3 move on the guiding cylinders 2. The height of the setting of the samples is set by the nut 9 moving along rod 7. With such an arrangement it is possible to set samples of different thickness so that their upper plane will always coincide with the inner surface of the sphere.

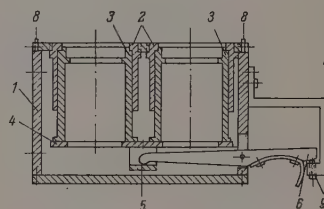


Fig. 3. Construction of the lower carriage.

To decrease the size of the light spot on the sample the mirror which directs the beam into the sphere is made concave with a radius of curvature of 300 mm. As a result of this the light spot is decreased to dimensions of $15 \times 8 \text{ mm}$ in the plane of the lower aperture of the sphere and $13 \times 6 \text{ mm}$ in the plane of the upper aperture.

The inside walls of the sphere are covered with barium sulfate. The pigment was mixed with a one percent solution of gelatin in water and deposited with a sprayer. The reflection spectrum of such a coating is shown in Fig. 4. The scattering indicatrix was also measured, and it was shown to differ only slightly from the indicatrix which follows the cosine law.

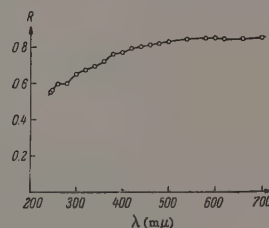


Fig. 4. Reflection spectrum of the sphere wall coating.

As can be seen from formula (2) the effectiveness of the sphere in the sense of light efficiency increases with decreasing sphere radius and increase of the reflection coefficient of its inside walls. It is possible to go along the line of decreasing sphere size only up to a given limit. This limit is determined by the requirement that the presence of the aperture and screen in the sphere have no noticeable effect on the results of measurements. The size of our sphere ($R = 60$ mm) satisfies this requirement.

The measurement of absolute coefficients of diffuse reflection proceeds in the following way. The sample in the carriage is set in the lower aperture of the sphere, the screen is set in the upper position, and the light beam is directed onto the wall of the sphere. The dark current is compensated; then the photomultiplier shutter is opened, bringing an unbalance to the electrical circuit—the microammeter needle departs from zero. By a change in the monochromator slit width the initial value of the anode current is restored (the needle is brought to zero) and by a rotation of the mirror the light beam is transferred to the sample and the screen is set at the lower position. The variation of anode current generated in the circuit by the last operations is compensated with an indicating potentiometer connected with a photometric scale, from which a reading of the reflection coefficient is obtained.

For transmission coefficient measurements, the lower aperture of the sphere is covered with a screen coated with barium sulfate and the sample is placed in one of the holes in the upper carriage. The initial placement of the carriage is such that its open hole is located against the upper aperture of the sphere. The light beam from the mirror is directed through this aperture into the sphere, and the movable screen is set in the upper position. After compensation of the dark current the photomultiplier shutter is opened and the balance upset by this is restored by changing the slit width. Then the carriage is moved into the other extreme position so that the sample to be measured is set over the opening in the sphere. The anode current in the circuit is thus changed and its restoration to its previous value proceeds by adjusting a calibrated potentiometer, on whose scale the transmission coefficient is read.

We have measured absolute values of reflection coefficients of a series of objects. Some of our results are shown in Tables 1 and 2.

The values of slit widths are shown in Table 1. It is easy to see that in the visible and ultraviolet spectral regions (to $300 \text{ m}\mu$) the slit width does not exceed that with which one must work in measuring transmission coefficients of nonscattering samples. Only in the $\lambda < 300 \text{ m}\mu$ region does the slit width increase.

In measurements of diffuse reflection and transmission coefficients of luminescent samples in the region of excitation bands, in addition to reflected (transmitted) light, there will also be luminescent light falling on the

Table 1

Wavelength (m μ)	Slit width (mm)	Diffuse reflection coefficient (%)				
		BaSO ₄	BaCO ₃	SrSO ₄	CaCO ₃	Gypsum powder
245	2.0	68.0	69.5	—	—	83.0
250	1.8	71.0	70.0	63.5	63.0	83.0
260	1.3	72.5	71.0	70.0	64.5	64.0
270	1.08	73.0	71.5	69.5	66.5	64.5
280	0.92	74.0	73.0	69.0	67.0	66.0
300	0.68	77.0	75.0	69.0	70.5	68.0
320	0.38	78.0	76.5	74.0	71.5	69.5
340	0.25	79.5	77.5	79.0	74.5	72.0
360	0.165	80.5	80.0	80.5	76.0	75.5
380	0.130	82.0	81.0	82.5	78.5	77.5
400	0.128	83.0	83.5	83.5	81.5	80.0
420	0.047	84.0	84.5	86.0	83.0	81.0
440	0.035	85.5	85.5	87.5	85.0	83.0
460	0.027	86.0	85.5	87.5	85.0	83.0
480	0.025	86.0	87.0	88.5	86.0	84.5
500	0.022	87.0	87.5	88.5	86.5	85.0
540	0.020	87.5	88.5	89.0	87.5	85.5
580	0.022	87.5	88.5	89.0	88.0	87.0
620	0.025	87.5	88.5	89.0	88.5	88.0
660	0.055	87.0	88.5	88.5	88.5	88.0
700	0.15	87.0	88.5	88.5	87.5	87.0

*Supplementary neutral filter used which attenuated the beam by a factor of five.

Table 2

Wavelength (m μ)	Diffuse reflection coefficient (%)						
	ZnO	TiO ₂		Silica gel	Quartz (44-53 μ)	Al ₂ O ₃ (44-53 μ)	
		Rutile	Anatase				
245	5.5	7.5	5.8	22.5	48.5	—	—
250	5.5	7.5	5.3	23.0	49.5	—	—
260	4.5	7.5	5.2	26.5	51.0	41.5	41.5
270	4.5	7.5	5.0	31.0	51.0	41.5	41.5
280	4.0	7.5	4.7	32.5	52.0	47.0	47.0
300	4.0	7.8	4.5	52.0	57.0	59.0	59.0
320	3.5	8.0	4.5	63.0	60.0	64.5	64.5
340	3.5	7.5	7.0	69.0	64.0	69.5	69.5
360	3.5	7.0	20.0	71.5	66.5	73.5	73.5
380	4.0	8.0	62.0	74.5	70.0	76.0	76.0
400	74.0	24.0	78.0	76.5	72.5	78.5	78.5
420	85.5	68.5	82.5	78.5	75.5	81.5	81.5
440	88.5	74.5	84.0	79.0	77.5	82.5	82.5
460	89.0	77.0	84.5	80.5	78.5	83.5	83.5
480	90.0	79.5	85.5	81.5	79.5	84.5	84.5
500	91.0	80.5	86.0	81.5	80.5	85.0	85.0
540	91.5	82.0	87.5	83.5	82.5	85.0	85.0
580	92.5	82.5	88.5	84.0	84.0	86.0	86.0
620	90.5	83.0	87.0	84.5	83.5	85.5	85.5
660	89.5	83.0	87.5	85.0	84.0	84.5	84.5
700	89.0	82.5	87.0	84.0	83.5	85.0	85.0

detector. As a result of this the values of coefficients can show a certain measure of increase. In cases in which the luminescent band is not overlapped by an excitation band it is possible to use a suitable light filter to exclude the luminescent light. In our device a place for such filters is provided. In Fig. 2 the filter holder 16 is shown adjacent to the photomultiplier shutter. In these same cases when overlap of the excitation and luminescent bands takes place, the measurement is made with a special spectrophotometer consisting of two monochromators. The first monochromator will serve for illuminating the samples with monochromatic light. Light reflected by the sample and luminescent light is passed through the second monochromator before falling on the detector. In this way only a small portion of the luminescent band is incident on the detector which coincides spectrally with the reflected light. Its intensity can be evaluated by a supplementary measurement with this same equipment.

In conclusion the author expresses thanks to M. G. Primakina for help in the work.

REFERENCES

1. A. S. Toporets, Zhur. Opt.-Mekh. Prom. No. 2, 20 (1958).
2. A. H. Taylor, Sci. Papers Natl. Bur. Standards 16, 421 (1920).
3. F. B. Huke, R. H. Heidel, and V. A. Fassel, J. Opt. Soc. Am. 43, 400 (1953).

SHORT COMMUNICATIONS

A METHOD OF DETERMINING SEPARATELY THE COEFFICIENTS OF ABSORPTION AND SCATTERING IN TURBID MEDIA

V. A. Timofeeva (pp. 533-534)

Received 11 July 1960

This paper describes an experimental verification of the method of determining separately the coefficients of absorption and scattering proposed fairly recently, on theoretical grounds, by Rozenberg.¹ Rozenberg attempted to find a theoretical basis for the empirical expressions that we obtained earlier when studying the depth conditions in turbid media; he obtained the equation:

$$\alpha = k' \bar{\mu}, \quad (1)$$

where α is the absorption coefficient for the medium, k' is the attenuation coefficient for completely scattered light and $\bar{\mu}$ is the integrated mean value of the quantity μ for a body, characterizing the angular distribution of luminance with depth of the scattering medium. We have:

$$\bar{\mu} = \frac{\int_{-1}^{+1} \mu B_{\varphi} d\mu}{\int_{-1}^{+1} B_{\varphi} d\mu}. \quad (2)$$

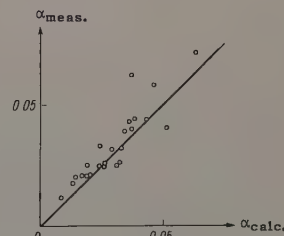
Here μ is the cosine of the scattering angle φ (the polar angle, defining the direction of the scattered light ray), B_{φ} is a quantity proportional to the luminance in the direction φ at a depth where the light is completely scattered. The numerator of Eq. (2) is "proportional to the radiation flux through a horizontal section, and the denominator to the flux which irradiates a spherical surface surrounding the observation point. Therefore both these quantities, and μ itself, can be measured directly by the use of a suitable array of photoelements."⁴

The derivation of Eq. (1) shows that it is valid for any medium as long as the depth conditions are fulfilled in determining $\bar{\mu}$. Consequently, this method is more general than the methods suggested earlier for the separate determination of the coefficients mentioned above. It is therefore very important to verify the method experimentally. To this end we have used our experimental data on the study of depth conditions of light in turbid media. We obtained from these data the quantities necessary for verifying Eq. (1), namely, the attenuation coefficients for completely scattered light, the absorption coefficients for several turbid media (colored and uncolored milky media³), and the quantities characterizing the shape of the polar diagrams for these media. Note that the absorption coefficient α of these turbid media is equal to the sum of the absorption coefficients α_d of the media due to the dye (nigrosine) and due to the tap water (averaging 0.01 cm^{-1}).

The methods of determining k' and α_d were described earlier^{2,5} and we will not discuss them here. To obtain $\bar{\mu}$ the numerator and denominator of Eq. (2) were evaluated by graphical integration. All the quantities mentioned above are given in the Table. The scattering coefficients of the turbid media are shown in the σ column; absorption coefficients calculated from Eq. (1) are

Serial No.	$\alpha_{\text{meas.}}$ (cm^{-1})	$\sigma_{\text{meas.}}$ (cm^{-1})	$k'_{\text{meas.}}$ (cm^{-1})	B_0	B_{30}	B_{45}	B_{60}	B_{90}	B_{120}	B_{150}	B_{180}	μ	$\alpha_{\text{calc.}}$ (cm^{-1})
1	0.026	1.7	0.102	71	64	50	31	17	12	11	0.31	0.032	
2	0.040	1.3	0.109	32	27	18	10	5	4	3.5	0.34	0.037	
3	0.071	1.3	0.155	135	119	80	42	21	1.5	1.4	0.41	0.063	
4	0.040	1.3	0.115	86	73	47	22	9	6	5	0.44	0.051	
5	0.032	1.1	0.092	137	124	88	55	31	23	20	0.32	0.029	
6	0.043	1.1	0.107	145	124	84	50	28	19	17	0.33	0.036	
7	0.058	1.1	0.127	61	53	35	19	9	7	6	0.36	0.046	
8	0.021	1.4	0.0765	120	109	84	56	35	26	24	0.26	0.020	
9	0.061	0.54	0.0827	84	64	32	15	9	5	3	0.45	0.037	
10	0.012	0.42	0.0338	59	54	38	26	17	13	12	0.25	0.0083	
11	0.018	0.42	0.0464	61	52	34	21	15	10	9	0.28	0.013	
12	0.020	1.3	0.0695	70	64	49	37	27	22	19	0.20	0.014	
13	0.025	1.3	0.0793	58	51	39	25	17	12	10	0.24	0.019	
14	0.026	1.3	0.0875	130	118	86	53	32	23	21	0.30	0.026	
15	0.039	1.2	0.0897	127	105	69	40	21	16	11	0.37	0.033	
16	0.021	1.1	0.0720	127	116	82	56	36	28	27	0.27	0.019	
17	0.025	1.1	0.0820	108	97	73	46	29	21	19	0.30	0.025	
18	0.025	1.4	0.0870	93	81	59	36	21	16	15	0.30	0.026	
19	0.032	1.4	0.0984	115	102	71	42	24	17	16	0.33	0.033	
20	0.044	1.4	0.111	133	108	75	43	23	16	14	0.34	0.038	
21	0.058	1.4	0.126	113	99	95	36	18	12	11	0.37	0.047	
22	0.021	0.54	0.0478	75	65	43	25	14	10	9	0.35	0.017	
23	0.025	0.54	0.0530	63	53	34	16	9	7	7	0.59	0.031	
24	0.033	0.54	0.0610	48	39	24	12	7	5	4.5	0.39	0.024	
25	0.044	0.54	0.0712	62	48	26	10.7	6	4.2	4	0.60	0.043	

given in the $\alpha_{\text{calc.}}$ column. Note that the values of B_{φ} obtained in different experiments are not reduced to a single photometer sensitivity (the subscript to B indicates the angle of scattering).



Comparison of the calculated and measured values of the absorption coefficients of turbid media.

In the Figure, the values of $\alpha_{\text{calc.}}$ are plotted on the axis of abscissas and those of $\alpha_{\text{meas.}}$ on the axis of ordinates. The results of the comparison are quite satisfactory, bearing in mind the natural scatter in the points due to measurement errors. An analysis of the results showed that the basic source of the scatter in the points is inaccuracy in determining $\bar{\mu}$, and, in particular, inaccuracy in determining the angular distribution of luminance for the directions $90^\circ \leq \varphi \leq 180^\circ$ (the effect of the walls of the vessel, obstruction of the medium by the photometer, etc.). Therefore, in determining the absorption coefficient of turbid media by Eq. (1), special attention must be paid to careful determination of the shape of the polar diagram of distribution of luminance in the given medium.

REFERENCES

1. G. V. Rozenberg, Opt. i Spekt. 5, 440 (1958).
2. V. A. Timofeeva, Izvest. Akad. Nauk SSSR, Ser. Geofiz. 23, 265 (1957).
3. V. A. Timofeeva, Doklady Akad. Nauk SSSR 113, 3, 556 (1957).
4. G. V. Rozenberg, Opt. i Spekt. 7, 407 (1959). Optics and Spectroscopy 7, 262 (1959).
5. V. A. Timofeeva, Trudy Morskogo Gidrofiz. Inst. Akad. Nauk SSSR 3, 35 (1953).

ON THE INFLUENCE OF VIBRATIONS ON THE LIMITING POLARIZATION OF THE LUMINESCENCE OF COMPLEX MOLECULES

S. I. Kubarev (pp. 535-537)

Received 25 July 1960

Up to the present time, the polarized luminescence of solutions of complex molecules has been interpreted with the help of the classical model of a linear oscillator which was first applied to complex molecules by Vavilov and Levshin.¹ The limiting value of the polarization in this model amounts to 0.5 for the long-wavelength band. However, it is well known that, even with the elimination of all external depolarizing factors, there has never been experimental success in obtaining this value for the limiting polarization.

Although Levshin² as early as 1924 discovered a certain diminution in the degree of polarization over the radiation spectrum when the excitation was in the long-wavelength absorption band, the view that the polarization did not change within the limits of the long-wavelength band subsequently continued to prevail. It has recently been shown in the works of Sevchenko and his collaborators³ that the degree of polarization within the limits of the long-wavelength band undergoes characteristic changes as a function of ν_{abs} and ν_{em} . These changes are particularly characteristic for semicomplex molecules.⁴ Analogous phenomena have been detected in phosphorescence spectra.⁵

In the present note, we shall show that the experimentally observed dependence of the polarization on ν_{abs} and ν_{em} may be explained by the dependence of the dipole moment of the electronic transition on the coordinates of the nuclei. We shall carry out the calculation with the help of the mathematical apparatus already used previously to examine certain problems of the spectroscopy of complex molecules.⁶

If we assume that the adiabatic approximation is applicable to the complex molecules under consideration, then we have the following expression for the dipole moment of the transition $am \rightarrow bn$, where a and b are indices of the electronic states and m and n of the vibrational states:

$$D_{am \rightarrow bn} = i \langle am | M_x | bn \rangle + j \langle am | M_y | bn \rangle + k \langle am | M_z | bn \rangle; \quad (1)$$

$$M_\alpha = \int \psi_b^*(q, R) \alpha \psi_a(q, R) dq; \quad \alpha = x, y, z.$$

Here x , y , and z comprise a coordinate system rigidly bound to the molecule. It follows from (1) that for each transition $am \rightarrow bn$ there corresponds a distinct direction of the dipole moment, and consequently a linear oscillator may be matched with each elementary transition $am \rightarrow bn$. As is well known,⁷ the limiting polarization for two oscillators (the absorbing and the radiating one) with an angle α between them equals

$$P(mn, sl) = \frac{3 \cos^2 \alpha - 1}{\cos^2 \alpha + 3}.$$

In our case, evidently, we have for $\cos \alpha$ the expression

$$\cos \alpha = \frac{M_{1x}(mn) M_{2x}(sl) + M_{1y}(mn) M_{2y}(sl) + M_{1z}(mn) M_{2z}(sl)}{\sqrt{M_{1x}^2 + M_{1y}^2 + M_{1z}^2} \cdot \sqrt{M_{2x}^2 + M_{2y}^2 + M_{2z}^2}}; \quad (3)$$

$$M_{1\alpha} = [am | M_\alpha | cn]; \quad M_{2\alpha} = [bs | M_\alpha | al].$$

M^{ac} corresponding to absorption (the transition $am \rightarrow cn$) and M^{ba} to radiation (the transition $bs \rightarrow al$).

The limiting polarization measured experimentally equals

$$P_0 = \frac{A_{v_{m,s}} \sum_{n,l} P(mn, sl) I_{mn} I_{sl}}{A_{v_{m,s}} \sum_{n,l} I_{mn} I_{sl}}; \quad (4)$$

$$\left. \begin{aligned} I_{mn} &= \{ \langle m | M_{1x} | n \rangle^2 + \langle m | M_{1y} | n \rangle^2 + \langle m | M_{1z} | n \rangle^2 \} \delta(E_{em} - E_{am} - h\nu_1); \\ I_{sl} &= \{ \langle s | M_{2x} | l \rangle^2 + \langle s | M_{2y} | l \rangle^2 + \langle s | M_{2z} | l \rangle^2 \} \delta(E_{bs} - E_{al} - h\nu_2). \end{aligned} \right\} \quad (5)$$

Here I_{mn} and I_{sl} are the spectral densities of absorption and radiation respectively; the symbol $A_{v_{m,s}}$ denotes the operation of averaging over the quantum numbers m and s .

It is not difficult to see under what conditions the "electronic oscillator" will "sense" the motion of the nuclei. First of all, if we set $M_1 = \text{const.}$ and $M_2 = \text{const.}$, then it is evident that $P_0 = \text{const.}$ In the general case, the carrying out of the operations of averaging and summation in formula (4) is a difficult task; however, if we take into account the fact that the quantity M is generally a smooth function of the nuclear coordinates, then this task becomes solvable. The smoothness of the variation of M is indicated above all by the small magnitude of the deviation from $P_0 = \text{const.}$ in the long-wavelength band. The measurement of the temperature dependence of the value of the zeroth moment, which characterizes the integrated intensity, might serve as another criterion of this (when the variation of M is smooth, there must be a very slight temperature dependence). Taking the foregoing into account, let us expand M_1 and M_2 in a series in the nuclear coordinates and confine ourselves to the first terms of the expansion. Then we obtain, for $P(mn, sl)$,

$$P(mn, sl) = P_0^0 + A_1 \frac{\langle m | R | n \rangle}{\langle m | n \rangle} + A_2 \frac{\langle s | R | l \rangle}{\langle s | l \rangle} + \dots; \quad (6)$$

$$\left. \begin{aligned} P_0^0 &= \frac{3(M_1^0 M_2^0)^2 - (M_1^0)^2 (M_2^0)^2}{(M_1^0 M_2^0)^2 + 3(M_1^0)^2 (M_2^0)^2}; \\ A_1 &= 20 \frac{(M_1^0 M_2^0)(M_1^0)^2 - (M_1^0 M_1^0)(M_1^0 M_2^0)}{[(M_1^0 M_2^0)^2 + 3(M_1^0)^2 (M_2^0)^2]^2}; \\ A_2 &= 20 \frac{(M_2^0 M_1^0)(M_2^0)^2 - (M_2^0 M_0^0)(M_1^0 M_2^0)}{[(M_1^0 M_2^0)^2 + 3(M_1^0)^2 (M_2^0)^2]^2}. \end{aligned} \right\} \quad (7)$$

Let us carry out the summation in (4) by making use of the procedure proposed by Lax.⁸ We shall write out only one representative term.

$$\begin{aligned} & A_{vm} \sum_n \langle m | M_{1x} | n \rangle^2 \frac{\langle m | R | n \rangle}{\langle m | n \rangle} \delta(E_{cm} - E_{cn} - \hbar \nu_1) \\ & \approx A_{vm} \sum_n \langle n | M_{1x} | m \rangle \langle m | R | n \rangle \delta(E_{cm} - E_{cn} - \hbar \nu_1) \cdot M_{1x}^0 \quad (8) \\ & = M_{1x}^0 \int \exp(-2\pi i \nu_1 t) dt \operatorname{Sp} \left(R e^{\frac{it}{\hbar} \hat{H}_c} M_{1x} e^{-\frac{it}{\hbar} \hat{H}_a} e^{-\beta \hat{H}_a} \right). \end{aligned}$$

The result may finally be written in the form

$$P_0 = P_0^0 + A_1 \frac{\int e^{-2\pi i \nu_1 t} dt \operatorname{Sp}(G_{1a})}{\int e^{-2\pi i \nu_1 t} dt \operatorname{Sp}(G_{1a})} + A_2 \frac{\int e^{-2\pi i \nu_2 t} dt \operatorname{Sp}(G_{2b})}{\int e^{-2\pi i \nu_2 t} dt \operatorname{Sp}(G_{2b})}, \quad (9)$$

where

$$\left. \begin{aligned} G_1 &= \sum_{a=s, y, z} M_{1a}^0 R e^{\frac{it}{\hbar} \hat{H}_c} M_{1a} e^{-\frac{it}{\hbar} \hat{H}_a}; \quad G = \sum_a M_{1a} e^{\frac{it}{\hbar} \hat{H}_c} M_{1a} e^{-\frac{it}{\hbar} \hat{H}_a}; \\ G_2 &= \sum_a M_{2a}^0 R e^{-\frac{it}{\hbar} \hat{H}_a} M_{2a} e^{\frac{it}{\hbar} \hat{H}_b}; \quad G_3 = \sum_a M_{2a} e^{-\frac{it}{\hbar} \hat{H}_a} M_{2a} e^{\frac{it}{\hbar} \hat{H}_b}. \end{aligned} \right\} \quad (10)$$

Here ρ_a and ρ_b are the vibrational distribution functions in the electronic states a and b . For $M_1 = M_2$, we obtain $A_1 = A_2 = 0$; i.e., it is necessary to take subsequent terms of the expansion into account. We note that $\hat{H}_c$, $\hat{H}_b$, and $\hat{H}_a$ are arbitrary operators; thus (9) gives an expression for the limiting polarization which contains, aside from the dependence on the absorption and radiation frequencies ν_1 and ν_2 , the temperature dependence as well.

As an illustration, let us examine a simple model. We shall consider that a single vibration exerts the fundamental influence on the limiting polarization. Let us suppose that this vibration may be approximated by a harmonic oscillator of frequency ω which does not change on going over to the excited electronic state. The calculation according to formula (9) may in this case be carried through to the end. For the correction depending on ν_1 we obtain

$$\left. \begin{aligned} P_0' &\sim (2n-1) + (1-n) \sqrt{\frac{n}{n+1}} \frac{I_{\sigma+1}(z)}{I_\sigma(z)} - n \sqrt{\frac{1+n}{n}} \frac{I_{\sigma-1}(z)}{I_\sigma(z)}; \\ z &= 2|w| \sqrt{n(1+n)}, \end{aligned} \right\} \quad (11)$$

where $I_\sigma(z)$ is the Bessel function for a pure-imaginary argument, $\sigma = 2\pi(\nu_1 - \nu_0)/\omega$, ν_0 is the frequency of the purely electronic transition, $\bar{n}$ is the Planck average, and $|w|^2$ is a quantity depending on the shift of the equilibrium positions of the oscillator in the ground and the excited electronic states. Let us consider the two limit-

ing cases of high and low temperatures. In the first case, $I_\sigma(z) \sim e^{z - (\sigma^2/2z)}$ and

$$\begin{aligned} P_0' &\sim Q_1 + Q_2 \sigma; \quad Q_1 = (2n-1) \\ &+ e^{-\frac{1}{2\sigma}} \left[(1-n) \sqrt{\frac{n}{1+n}} - n \sqrt{\frac{1+n}{n}} \right]; \\ Q_2 &= \left[(n-1) \sqrt{\frac{n}{1+n}} - n \sqrt{\frac{1+n}{n}} \right] \frac{e^{-\frac{1}{2\sigma}}}{z}. \end{aligned}$$

For low temperatures, $I_\sigma(z) \sim (z/2)^\sigma / \sigma!$ ($z \ll \sigma$) and

$$P_0' \sim (2n-1) + (1-n) \sqrt{\frac{n}{1+n}} \frac{z}{2(\sigma+1)} - n \sqrt{\frac{1+n}{n}} \frac{2\sigma}{z}.$$

In those cases when it is necessary to take account of the contribution from many degrees of freedom, the method of moments^{6,8,9} comes to our assistance.

Taking account of the complexity of the system, one may employ asymptotic expansions of the Edgeworth type.⁸ Then analysis of formula (9) may lead to the entire set of properties noted for the polarization.³ This confirms that complex molecules may be considered from a single point of view in relation to polarization also.

Although the value which we have calculated for the vibrational depolarization has the character of a correction, it is just this value which directly reflects the connection of the structural properties of the molecule with its optical properties. Since, according to formula (9), $P_0 = P_0(\nu_1, \nu_2, T)$ and in the high temperature approximation $P_0 = P_0^0 + \bar{A} \cdot T$, then in certain cases it is perhaps appropriate to introduce the corresponding corrections in the Levshin-Perrin formula, which may substantially change the results of a number of computations (for example, that of the molar volume, v , with the help of the indicated formula).

REFERENCES

1. S. I. Vavilov and V. L. Levshin, *Z. Physik* **16**, 136 (1923); S. I. Vavilov. *Sobr. soch.* (Collected papers), Vol. 1, p. 129, Izd. Akad. Nauk SSSR, 1952.
2. V. L. Levshin, *Z. Physik* **26**, 274 (1924).
3. A. N. Sevchenko, G. P. Gurinovich, and A. M. Sarzhenskii, *Doklady Akad. Nauk SSSR* **126**, 979 (1959); *Ibid.* **127**, 1191 (1959), *Soviet Phys.-Doklady* **4**, 644 (1959); *Ibid.* **4**, 867 (1960).
4. G. P. Gurinovich and K. N. Solov'ev, *Doklady na XIII Soveshchaniya Spekt.* (Proc. XIII Conf. Spectroscopy), Leningrad, 1960.
5. V. A. Pilipovich, *Kand. diss.*, Minsk, 1958.
6. S. I. Kubarev, *Doklady Akad. Nauk SSSR* **130**, 1067 (1960), *Soviet Phys.-Doklady* **4**, in press.
7. P. P. Feofilov, "Polyarizovannaya lyuminesentsiya atomov, molekul i kristallov" (Polarized Luminescence of Atoms, Molecules, and Crystals). Gosudarst. Izd. Fiz.-Mat. Lit., Moscow, 1959.
8. M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).
9. R. Kubo and I. Toyozawa, *Progr. Theoret. Phys.* (Kyoto) **13**, 160 (1955). (Translation in the collection: "Problemy fiziki poluprovodnikov" (Problems in the Physics of Semiconductors). Izd. Inostrannoi Lit., Moscow, 1957).

ABSORPTION OF LIQUID WATER IN THE LONG-WAVELENGTH PART OF THE INFRARED SPECTRUM (42-2000 μ)

A. E. Stanevich and N. G. Yaroslavskii (pp. 538-539)

Received 24 September 1960

The study of the optical properties of ordinary and "heavy" water in the near and intermediate parts of the infrared spectrum (0.8-42 μ), the investigation of the absorption spectrum of water, and a consideration of its general nature have been the subject of numerous studies (see, for example, refs. 1-9). There has consequently been careful investigation of the microwave absorption of liquid water,¹⁰⁻¹² indicating a spectrum of relaxation times in the Debye absorption region centered around 1 cm. However, there has been extremely little investigation in the intermediate and long wavelength regions of the infrared spectrum. Scattered experimental studies to determine the absorption of liquid water in this region include those of Rubens^{13,14} and of Cartwright.¹⁵⁻¹⁸ In these investigations, based on the use of the "residual light" method for the production of monochromatic radiation, measurements were made of the absorption by liquid ordinary and "heavy" water in spectral regions in the neighborhood of 52, 63, 83, 92, 109, 117, 152, and 313 μ . In these investigations the precision of the results obtained by the authors is reported as lower than that possible for the "residual light" method.

Kislovskii,¹⁹ using data on the absorption and reflection of water in the near and intermediate regions of the infrared spectrum, and also data on the absorption of water in the microwave region, on the basis of models developed by him carried out calculations of the optical constants of liquid ordinary water over a very wide range of the electromagnetic spectrum, for wavelengths from 2 μ to 100 km. However, direct experimental data on the absorption of liquid ordinary and "heavy" water in the long wavelength regions of the infrared spectrum (for $\lambda \gg 300 \mu$) are not available at the present time.

The aim of the present work is the investigation of the absorption of liquid (ordinary and "heavy") water in the extreme long wavelength region of the infrared spectrum and the refinement of the data of Rubens and Cartwright in the region up to 300 μ .

The work was carried out with the help of the pre-

viously described vacuum long wavelength spectrometer DIKS-1.²⁰⁻²²

The continuous curves in Fig. 1 show the variation, in the wavelength region from 42 to 2000 μ (or of wave numbers from 240 to 5 cm^{-1}), of the percent transmission (T) and the optical density (D) of liquid ordinary water in a layer of thickness 13 μ at room temperature. The dotted curve on this same graph corresponds to the specific absorbance k, calculated from the equation

$$k = \frac{\lambda \ln \frac{1}{T}}{4\pi d},$$

where T is the percent transmission in arbitrary units, λ is the wavelength in microns, and d is the thickness of the absorbing layer in microns.

Analogous curves for "heavy" water in the wave number region 240-10 cm^{-1} (42-1000 μ) are shown in Fig. 2.

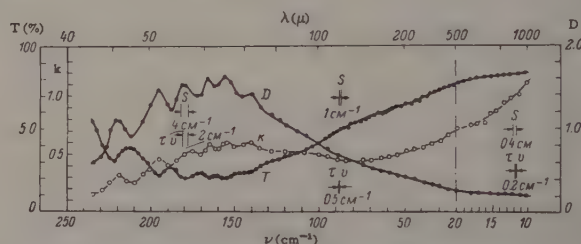


Fig. 2. Transmission (T), optical density (D), and specific absorbance (k) for liquid "heavy" water for a layer thickness of 0.013 mm in the region 42-1000 μ .

The data on the transmission by ordinary and "heavy" water is presented in Figs. 1 and 2 by the points indicated on the diagrams, which were obtained by calculations from two spectrograms, one of which was obtained on the DIKS-1 apparatus with the light beam passing through an empty quartz cell, and in the other case through a quartz cell filled with water. The thickness of the water layer, found to be 13 μ , was determined by an interferometric method in the near infrared spectral region on an IKS-12 spectrometer using a lithium fluoride prism. Discrepancies in the observed transmissions in various overlapping regions obtained by the use of different echelettes did not exceed 5%. For the construction of the transmission curves (Figs. 1 and 2) we used average values of the transmission obtained in two, or occasionally in a larger number, of measurements.

A comparison of our data on the absorption of liquid ordinary and "heavy" water with the results of Rubens and Cartwright¹³⁻¹⁸ shows that the agreement is best at wavelengths 52, 152, and 313 μ . The differences in the values of the transmission of water obtained at other parts of the spectrum are as much as several percent. Figures 1 and 2 show that the broad absorption band in

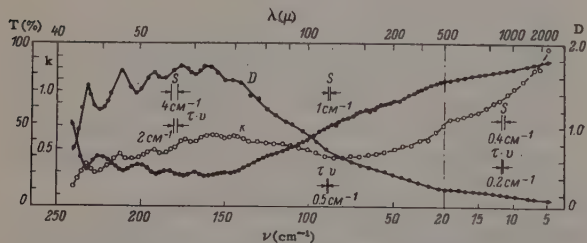


Fig. 1. Transmission (T), optical density (D), and specific absorbance (k) for liquid water at a layer thickness of 0.013 mm in the region 42-2000 μ . S = spectral slit width (6 cm^{-1}); $\tau\nu$ = product of the time constant (in sec) of the input amplifier and the sweep rate (in $\text{cm}^{-1}/\text{sec}$).

the spectrum of liquid ordinary and "heavy" water centered around 60μ (175 cm^{-1}) is not simple but rather exhibits a structure with many weak absorption maxima, which can be ascribed to vibrations of complexes of water molecules, held together by hydrogen bonds. The wave numbers of these absorption maxima for liquid ordinary water are at 232, 210, 191, 175, 160, and 145 cm^{-1} , and for heavy water at 221, 196, 181, 166, 156, and 140 cm^{-1} .

In the wavelength region from 1000 to 2000μ , the spectral curve for the specific absorbance, k , of ordinary water, obtained from our measurements (Fig. 1) agrees within the limits of experimental error with the values calculated for water from measurements made in the microwave spectral region.^{19,23}

REFERENCES

1. N. E. Dorsey, "Properties of Ordinary Water Substance." Reinhold, New York, 1940.
2. M. Sohn, Z. Physik **116**, 34 (1940).
3. E. R. Blont and H. Lenormant, J. Opt. Soc. Am. **43**, 1093 (1953).
4. E. K. Plyler and N. Acquista, J. Opt. Soc. Am. **44**, 505 (1954).
5. E. Greinacher, W. Lüttke, and R. Mecke, Z. Elektrochem. **59**, 23 (1955).
6. P. A. Giguere and K. B. Harvey, Can. J. Chem. **34**, 798 (1956).
7. M. Ceccaldi, M. Goldman, and E. Roth, Proc. Colloq. Spectroscop. Intern. **6**, 623 (1957).
8. M. O. Bulanin, Opt. i Spektr. **2**, 557 (1957).
9. M. Ceccaldi, Rev. universelle mines **15**, 430 (1959).
10. I. A. Saxton, Proc. Roy. Soc. **A213**, 473 (1952).
11. I. A. Lane and I. A. Saxton, Proc. Roy. Soc. **A213**, 400 (1952).
12. E. H. Grant, T. I. Buchanan, and H. F. Cook, J. Chem. Phys. **26**, 156 (1957).
13. H. Rubens and E. Ladenburg, Verhandl. phys. Ges. **11**, 16 (1909).
14. H. Rubens, Verhandl. phys. Ges. **17**, 315 (1915).
15. C. H. Cartwright, Nature **135**, 872 (1935).
16. C. H. Cartwright, Nature **136**, 181 (1935).
17. C. H. Cartwright and I. Errera, Proc. Roy. Soc. **A154**, 138 (1936).
18. C. H. Cartwright and I. Errera, Phys. Rev. **49**, 470 (1936).
19. L. D. Kislovskii, Opt. i Spektr. **7**, 311 (1959), Optics and Spectroscopy **7**, 201 (1959).
20. H. G. Yaroslavskii, B. A. Zheludov, and A. E. Stanevich, Opt. i Spektr. **1**, 507 (1956).
21. H. G. Yaroslavskii and A. E. Stanevich, Opt. i Spektr. **5**, 384 (1958).
22. H. G. Yaroslavskii and A. E. Stanevich, Opt. i Spektr. **7**, 626 (1959), Optics and Spectroscopy **7**, 380 (1959).
23. M. Magat, J. Chem. Phys. **45**, 91 (1948).

REGISTRATION OF TIME-RESOLVED CONTOURS OF SPECTRAL LINES BY MEANS OF AN ELECTRON-OPTICAL CONVERTER

I. F. Balashov, M. P. Vanyukov, V. R. Muratov, and E. V. Nilov (pp. 540-541)

Received 14 October 1960

It has been shown in ref. 1 that an electron-optical converter can be used to register time-resolved spectra of the radiation emitted from different sections of a spark discharge channel. In this note, the results of an application of this method to the registration of time-resolved contours of spectral lines are reported.

The electron-optical method of registration of a spectrum is more sensitive than the photographic method; it permits registration of contours of spectral lines emitted during a single flash. This is not possible if photomultipliers are used for this purpose.²⁻⁴ To illustrate the feasibility of this method the contour of the hydrogen line H_{α} in the luminescence of a spark discharge was registered; to produce this discharge, a capacity of $0.5 \mu\text{f}$, an inductance of $0.5 \mu\text{h}$, a potential of 10.5 kv, and hydrogen pressure of 3.5 atm were employed; the distance between the electrodes was 3.5 mm. The setup used to perform this registration was arranged according to the scheme described in ref. 1. In this setup a spectrograph of the type SP-51 was used with a camera of focal length 800 mm. The electron-optical converter with the intensity amplifier was switched on by impulses of length $1 \mu\text{sec}$ at different times after the beginning of the discharge. The

image of the spectral line was photographed (scale 1:1) from the screen of the electron-optical converter on a film of sensitivity 65 units GOST by means of photo-objectives of f-number 1:1.5.

If the discharge channel is projected on the entrance slit of the spectrograph in such a way that its axis is perpendicular to the slit, then sections of the spectral line differing in height will characterize radiation from different sections of the channel. In Fig. 1, photographs of the contour of the line H_{α} are shown; they are obtained with an exposure time of $1 \mu\text{sec}$, at the times 0, 5, and $10 \mu\text{sec}$ after the beginning of the discharge. It appears from this figure that the luminescence of the spark discharge channel in hydrogen is mainly located in two zones—a central one and a peripheral one—which are separated from each other by a weakly luminous domain. Figure 2 shows the intensity distribution of the luminescence across the channel. This characteristic of the luminescence of the spark discharge in hydrogen has been reported by a number of investigators,⁵ but has so far not been explained in a definitive way. The asymmetry in the luminescence of the channel is noticeable even in the earlier stages of its development.

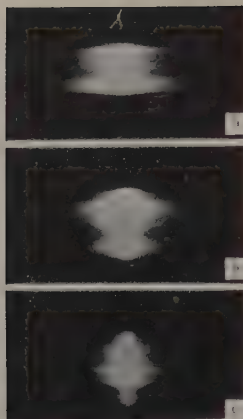


Fig. 1. Radiation of the H_{α} -line in a spark discharge in hydrogen (exposure time 1 μ sec). Time after the beginning of the discharge (in μ sec): a-0; b-5; c-10.

A photometric study of the photographs obtained permitted the construction of contours of the H_{α} -line for the different zones of the luminescence of the channel for various stages of development of the discharge. Figure 3 shows the H_{α} -line contour for the central zone of the channel during the earliest time interval considered in the investigation; the width due to the apparatus was 4 Å. At this stage of the discharge the half-width of the H_{α} -line is 43 Å for the central zone, and 38 Å for the peripheral zone. According to an estimate based on Holtsmark's statistical theory of line broadening, this width corresponds to an ion concentration of the order of magnitude $3 \times 10^{17} \text{ cm}^{-3}$. If the plasma gets cooler, and if the concentration of charged particles decreases, the line width decreases.

We would like to point out that not all the possibilities of the electron-optical method have been utilized in our experiments. Preliminary calculations show that the use of a converter of maximal sensitivity,⁶ in the case of radiation intensity corresponding to the domain of brightness saturation,⁷ would permit registration of the spectral line contour with a spectral resolution of 0.1 Å at an exposure time of 1 m μ sec.

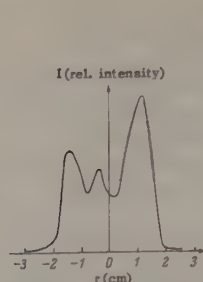


Fig. 2

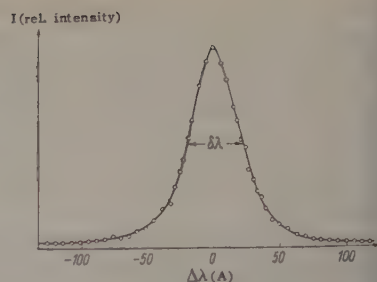


Fig. 3

Fig. 2. Intensity distribution of the luminescence (center of the H_{α} -line) across the channel of the spark discharge in hydrogen. Obtained by photometrical evaluation of the spectrum (see Fig. 1, a).

Fig. 3. Contour of the H_{α} -line emitted by the central zone of the channel (Fig. 1, a). $\delta\lambda = 43 \text{ Å}$.

REFERENCES

1. I. F. Balashov, M. P. Vanyukov, V. R. Muratov, and E. V. Nilov, *Opt. i Spekt.* **9**, 790 (1960), *Optics and Spectroscopy* **9**, 416 (1960).
2. M. P. Vanyukov and L. D. Khazov, *Doklady Akad. Nauk SSSR* **92**, 523 (1953).
3. B. A. Ermakov and A. A. Mak, *Priboiy i Tekh. Eksptl.* No. 3, 94 (1959).
4. M. P. Vanyukov, B. A. Ermakov, A. A. Mak, and V. R. Muratov, *Vestnik Leningrad. Gosudarst. Univ., Ser. Fiz. Khim.* No. **16**, 25 (1959).
5. I. M. Meek and I. D. Craggs, "Electrical Breakdown of Gases," Oxford Univ. Press, 1953.
6. M. M. Butslov, E. K. Zavoiskii, A. A. Kalinyak, V. B. Nikonov, V. V. Prokof'eva, and G. E. Smolkin, *Doklady Akad. Nauk SSSR* **121**, 815 (1958), *Soviet Phys.-Doklady* **3**, 693 (1959).
7. M. P. Vanyukov and A. A. Mak, *Uspekhi Fiz. Nauk* **66**, 301 (1958), *Soviet Phys.-Uspekhi* **1**, 137 (1959).

PHOTOELECTRIC SPECTROPOLARIMETER

V. A. Kizel' and V. I. Permogorov (pp. 541-543)

Received 31 October 1960

The apparatus described was constructed in order to measure the magnitude and dispersion of natural optical activity and magnetic rotation, but may also be used for any other measurement at full polarization.

The apparatus is single beam, the measurement being made by the null method; i.e., setting on the minimum intensity of light, which has passed through the polarizer, the sample under investigation, and the analyzer, the light signal is measured photoelectrically. The superiority of the null method is universally known: the influence of instability in the light source is removed, as is instability in the amplification coefficient of the electronic circuit, and most important in our case, variation in the transmission of light through the test sample is disposed of. In order to increase the accuracy of the minimum setting, a modulation system was used giving an oscillation of the plane of polarization about the null position, thus being a well-known analog of the half-shadow arrangement in visual apparatus. The superiority of alternating current amplification is well known.

A block diagram of the apparatus is shown in the figure. A filament lamp or a krypton lamp DKSSh serves as the light source (depending upon the region of the spectrum being studied). In our apparatus, the monochroma-

tor UM-2 was used. Prisms of Glan type with face dimensions of 15×15 mm serve the functions of polarizer and analyzer. Frequent diaphragming of the light beam inside the monochromator and keeping the diameter of the light beam down to 8 mm all along its subsequent path lowered the level of scattered light, which is a matter of extreme importance (see below). The image of the exit slit is projected onto the cathode of the photomultiplier.

The light coming out of the polarizer is modulated in the Faraday cell, fed with an impressed signal at a frequency of $\nu = 485$ cps from a special generator. Supposing the sample does not rotate the plane of polarization, then the light comes out of the analyzer, crossed to the polarizer, modulated with frequency 2ν . For an effective rotation, an unbalance signal with frequency ν appears. This latter signal manifests itself in the receiver-amplifier system composed of the FEU-29 photomultiplier with narrow band amplifier, tuned to a frequency ν (band width 15 cyc/sec), a synchronous detector, and the indicating microammeter μA as output. Such a scheme permits a considerable decrease in the effect of noises associated with the photomultiplier and amplifier. Covering shields of iron and copper protect the electronic circuit and photomultiplier against interference. The modulation frequency chosen is convenient for avoiding power-line pickup.

The process of measurement consists of turning the polarizer so that the output μA goes to a minimum (the angle of rotation is read off to an accuracy of 0.001°). The analyzer remains fixed in order to avoid variations in sensitivity of the photocathode with variations in polarization.

The amplitude of the oscillations of the plane of polarization in the Faraday cell is determined by the following considerations. For a crossed polarizer and analyzer the measured light flux is determined by the expression

$$I_{\text{meas.}} = I_{\text{sc.}} + I_0 \sin^2 \alpha,$$

where α is the angle of rotation of the modulator, I_0 is the intensity of light falling on the analyzer, and $I_{\text{sc.}}$ is the intensity of light scattered in the analyzer and before it. The latter may be set equal to

$$I_{\text{sc.}} = aI_0 + bI_{\text{meas.}}$$

Then the unbalance signal for a unit angle of rotation will be determined by the expression

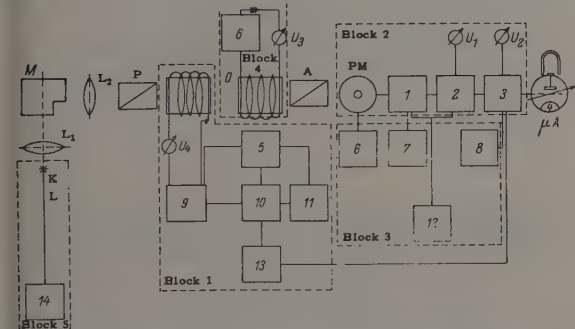
$$S = \frac{\Delta I_{\text{meas.}}}{\Delta \alpha} = \frac{I_0}{1-b} \sin 2\alpha.$$

Experience shows that the photomultiplier is the primary source of noise in the receiving system. Therefore it is possible to take

$$S_{\text{noise}} = cI_{\text{meas.}}^2.$$

It is possible to characterize the signal-to-noise ratio of the apparatus by the quantity

$$A = \frac{S}{S_{\text{noise}}} = \frac{\sin 2\alpha}{(a + \sin^2 \alpha)^2} \cdot \frac{1-b}{I_0 c}.$$



Block diagram of the apparatus. Block 1—modulator; block 2—registration system; block 3—registration system power supply; block 4—Faraday coil; block 5—light source L (incandescent lamp) or K (krypton lamp); M—monochromator; L₁, L₂—lenses; P, A—polarizer and analyzer, respectively; O—object under investigation; PM—photomultiplier; 1—preamplifier; 2—narrow band amplifier; 3—synchronous detector; 4—microammeter (vacuum tube instrument); 5—modulation generator supply; 6—preamplifier supply; 7—preamplifier supply; 8—supply of synchronous detector, converter and power amplifier; 9—power amplifier for modulation generator; 10—preamplifier; 11—master generator; 12—filament regulator; 13—phase shift control unit; 14—light source supply; U₁—coarse null indicator; U₂—fine null indicator; U₃—magnet current meter; U—amplitude modulation meter.

Finding the maximum, we have thus, for example, for $a = 0.01$, $\alpha_{\max} \sim 3^\circ$, while for $a = 0.1$, $\alpha_{\max} \sim 15^\circ$ and $A_{0.01} = 2A_{0.1}$. It is apparent then how important is the removal of scattered light.

Thus the scheme of modulation which was selected (see refs. 1, 2, 5) permits the selection of optimal conditions for each case by varying the current in the cell. This advantage distinguishes it, for example, from the modulation by rotating biquartz,³ for which the angle of rotation is fixed. The last method is inconvenient also for several other reasons: the higher demands—for our greater accuracy of measuring—upon the rotating synchronous motor, the necessity for a high speed transmission, vibration, etc. Modulation by some sort of shutter is even less convenient, since in this case the disadvantages just mentioned are accompanied by loss of light during the time when the beam is interrupted and a lowering of accuracy because $\alpha = 0$.

As a medium in the cell we used a liquid in a thin walled cuvette, which is more preferable than, for example, a core of glass because there are considerable difficulties in avoiding scattering the depolarization in the glass from the smallest imperfections and inhomogeneities, and also a certain double refraction from it. Moreover, the use of glass does not permit operating in the short wavelength region of the spectrum. For the visible region we used a cuvette with α -Bromonaphthalene, which has a large Verdet constant (the substance being doubly distilled under vacuum by the method of Martin, after which the cuvette is sealed off). It is of very great importance that the windows of the cuvette for the Faraday cell and for the liquid under investigation be without double refraction. We took special measures in order to avoid temperature gradients and convection currents in the cuvette. In the apparatus described the value $\alpha = 4^\circ$ was obtained for a current of 1 amp. The possi-

bility was also foreseen of reaching a minimum with the help of a second compensating Faraday tube, but this requires accurate temperature control and calibration and raises the amount of scattered light.

The apparatus is assembled on the base of an OSK-2 bench and is provided with a coil which permits measurements of the Faraday effect on the sample (field ~ 1800 oe) and is fed with a strong battery. It is possible to estimate the accuracy of the setting at the minimum signal from the following data: the signal corresponding to an unbalance of 1' exceeds the noise level by a factor of 10, which permits, with certainty, producing measurements with an accuracy of 0.003° (dials and other portions of a two-second theodolite were used). The power of the light of the apparatus permitted making measurements with this accuracy on samples with optical density up to 0.8. With a reduction in accuracy to 0.02° , it was possible to obtain measurements for densities up to 1.5-2. (These data correspond to a spectral band width equal to 20 Å at 4000 Å and 300 Å at 8000 Å. For an ordinary dispersion curve such an interval satisfies the restrictions given in ref. 4.)

In the preparation of the apparatus we received the assistance of G. I. Gorchakov and V. I. Letakhov. The generator was designed and tuned under the direction of Yu. V. Denisov. We express to them our sincere thanks.

REFERENCES

1. M. Billardon, *Compt. rend. acad. sci.* **248**, 2466 (1959).
2. S. Inoué and C. J. Koester, *J. Opt. Soc. Am.* **49**, 556 (1959).
3. E. Gillham, *J. Sci. Instr.* **34**, 435 (1957).
4. T. Gaume, *Rev. opt.* **37**, 242 (1958).
5. J. Badoz, *J. Phys. Radium* **17**, 143a (1956).

EFFECT OF p-TOLUIDENE AND POTASSIUM IODIDE ON THE FLUORESCENCE AND PHOTO-OXIDATION OF 9,10-di-n-PROPYLANTHRACENE

T. M. Vember and A. S. Cherkasov (pp. 544-546)

Received 3 November 1960

An investigation of the effect of p-toluidene and potassium iodide on the rate of photochemical oxidation of 9-methyl-10-methoxymethylanthracene^{1,2} has shown that these two substances have a different effect on the intermediate stage in the photochemical conversion. The photo-oxidation of anthracene derivatives has been assumed to proceed through the intermediate formation of triplet molecules and an unstable photooxide AOO,³ and therefore the following cases of possible effect of fluorescence quenchers (T) on the photo-oxidation were examined:

		Relative rate constants
I.	$^1A + T \rightarrow A + T$	m
II.	$^1A + T \rightarrow ^3A + T$	m
a.	$^3A + T \rightarrow A + T$	m_1
b.	$AOO + T \rightarrow A + TOO$	m_2

It has been established that p-toluidene deactivates the singlet-excited molecules of (^1A) 9-methyl-10-methoxy-

methylanthracene and interacts with the intermediate photo-oxide, liberating the initial substance (both processes produce a decrease in the rate of photo-oxidation). Potassium iodide quenches the fluorescence with a conversion of singlet-excited molecules to triplet-excited (^3A), which produces an increase in the quantum yield of photo-oxidation, and also participates in some processes leading to a decrease in the quantum yield of photo-oxidation. However, it is not possible to determine, from the available experimental data, whether this deactivation influence of KI is connected with the partial deactivation of ^1A during quenching, with the deactivation of ^3A , or with the interaction of KI and AOO.

In the present work, the effect of these fluorescence quenchers on the quantum yields of fluorescence and photo-oxidation of 9,10-di-n-propylantracene was investigated. The latter differs from methylmethoxymethylanthracene in that concentration fluorescence quenching

alcohol solutions is absent and KI has little quenching effect on its fluorescence.*

We discovered the absence of concentration quenching and quenching by potassium iodide in alcohol solutions of other 9,10-dialkyl derivatives of anthracene (9,10-dimethyl- and 9,10-diethylantracene). The fluorescence of 9,10-phenylantracene is not concentration quenched but is markedly quenched by potassium iodide.

All experiments were carried out in alcohol solutions. Photodimers of 9,10-dipropylantracene do not form (in an oxygen-free atmosphere it does not react photochemically) and only the photo-oxidation reaction occurs during irradiation of its solutions. The absorption and fluorescence spectra (in the working region of wavelength) are not changed upon addition of the studied quenchers. Methods of determining the quantum yields of fluorescence (Φ_f) and photo-oxidation (P_F) have been described in refs. 2 and 4.

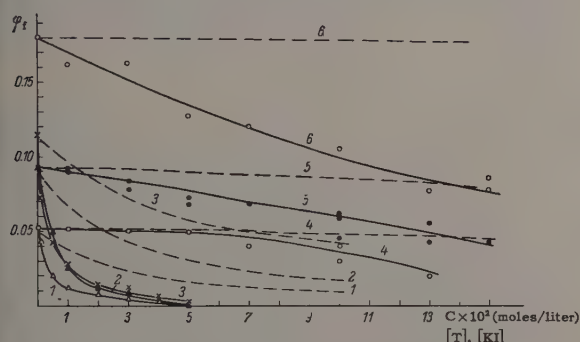


Fig. 1. Dependence of the photo-oxidation quantum yields of 9,10-di-n-propylantracene (P) on the concentration of p-toluidene (T) (curves 1-3) and potassium iodide (KI) (curves 4-6). Concentration (in moles/liter): curves 1,4— $[P] = 1.5 \times 10^{-3}$, $[O_2] = 1.3 \times 10^{-3}$; curves 2,5— $[P] = 3 \times 10^{-3}$, $[O_2] = 1.3 \times 10^{-3}$; curve 3— $[P] = 1.5 \times 10^{-3}$, $[O_2] = 6.4 \times 10^{-3}$; curve 6— $[P] = 3 \times 10^{-3}$, $[O_2] = 6.4 \times 10^{-3}$. The broken line represents the dependence of the change of photo-oxidation quantum yields on the concentration of quencher calculated on the assumption regarding their proportionality to the fluorescence quantum yields.

The investigation showed that p-toluidene and KI quench the photo-oxidation to a considerably larger degree than the fluorescence (Fig. 1). Comparison of the experimental data obtained from toluidene with values calculated using an expression for the photo-oxidation quantum yield, resulting from different variations in the effect of the quencher,¹ showed that toluidene affects the photo-oxidation of dipropylantracene and methylmethoxymethylantracene in a similar manner. During its interaction with a singlet-excited molecule, the singlet state does not convert to the triplet state (process I),*

*The necessity of assuming this process results from the observed good linear dependence of the ratio of experimentally obtained values Y/P_F on concentration quenching (analogous to ref. 2).

and the interaction of toluidene with the intermediate photo-oxide leads to liberation of the initial substance (process b). It is evident, from Fig. 2, that the relations

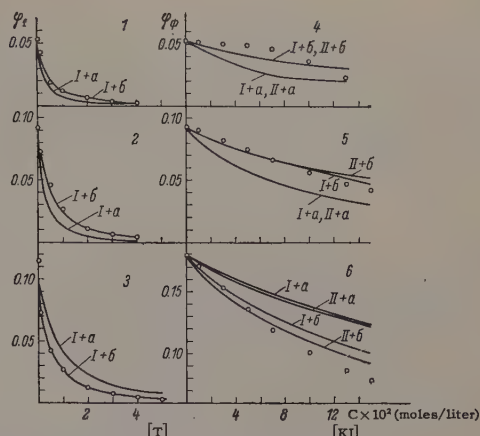


Fig. 2. Experimental (points) and calculated (lines) dependencies of the quantum yields of photo-oxidation of 9,10-di-n-propylantracene (P) on the concentrations of p-toluidene (curves 1-3) and potassium iodide (curves 4-6). Concentration (in moles/liter): curves 1,4— $[P] = 1.5 \times 10^{-3}$, $[O_2] = 1.3 \times 10^{-3}$; curves 2,5— $[P] = 3 \times 10^{-3}$, $[O_2] = 1.3 \times 10^{-3}$; curve 3— $[P] = 1.5 \times 10^{-3}$, $[O_2] = 6.4 \times 10^{-3}$; curve 6— $[P] = 3 \times 10^{-3}$, $[O_2] = 6.4 \times 10^{-3}$. The indexes I + a, II + a, I + b, and II + b denote the processes (see above-mentioned scheme), which are considered in the calculation.

obtained from the expression for P_F , which correspond to this variant (I + b),

$$\Phi_f = \frac{\frac{t}{f+t} + \frac{q}{f+t} [O_2]}{1 + \frac{q}{f+t} [O_2] + \frac{m}{f+t} [T]} \cdot \frac{\frac{k_2}{k_1} [O_2]}{1 + \frac{k_2}{k_1} [O_2]} \cdot \frac{\frac{k_4}{k_3} [A]}{1 + \frac{k_4}{k_3} [A] + \frac{m_2}{k_3} [T]}$$

are in good agreement with the experiment (at $m_2/k_3 = 203$). Values of the constants (determined by a method described in refs. 1 and 3)* which were used in the cal-

*For the designation of constants see refs. 1 and 3.

culations are presented in the Table.

$\frac{t}{f+t}$	$\frac{p}{f+t}$	$\frac{q}{f+t}$	$\frac{m}{f+t}$	$\frac{h_1}{h_2}$	$\frac{h_1}{h_3}$
0.04	0	448	$\frac{T}{KI}$	20000	104
			63	1.4	

The results obtained in studying the effect of KI on the quantum yields of fluorescence and photo-oxidation of dipropylantracene are interesting in that the relation which permits the problem to be solved is not clear from the results obtained in studying methylmethoxymethylantracene: it is possible that the decrease in photo-oxidation quantum yield is connected with an interaction of KI and the intermediate photo-oxidation products. Actually, the significant decrease in photo-oxidation quantum yield in the presence of KI, and the almost complete absence of fluorescence quenching (Fig. 1), indicates that, in the stated instance, the inhibition of photo-oxidation is connected with deactivation of the intermediate

products. It is evident from Fig. 2 that the most suitable expressions for describing the experimental results are those for P_F , which were obtained on the assumption concerning the presence of the interaction of KI with the intermediate photo-oxide, i.e., that process which it is necessary to consider for describing the experimental data

obtained with toluidene (Fig. 2). However, the discrepancy of calculated and experimental dependencies is significantly larger in the case of KI than in the case of toluidene. This discrepancy possibly depends on some interaction processes of KI and the intermediate photo-oxidation products not considered in the investigated scheme.

REFERENCES

1. A. S. Cherkasov and T. M. Vember, Opt. i Spektr. 7, 321 (1959), Optics and Spectroscopy, 7, 207 (1959).
2. T. M. Vember and A. S. Cherkasov, Izvest. Akad. Nauk SSR, Ser. Fiz. 24, 577 (1960).
3. A. S. Cherkasov and T. M. Vember, Opt. i Spektr. 6, 503, (1959), Optics and Spectroscopy 6, 319 (1959).
4. A. S. Cherkasov and T. M. Vember, Opt. i Spektr. 4, 203 (1958).

SPECTROSCOPIC DETERMINATION OF ION MOBILITIES IN MIXTURES OF RARE GASES

V. M. Zakharova and Yu. M. Kagan (pp. 547-548)

Received 3 November 1960

1. The spectroscopic method has often been used for measuring the drift velocities of gaseous ions under the conditions existing in the positive column of a self-sustaining discharge.^{1,2} In the present investigation, this method is used to study ion mobilities in the positive column of a discharge in the binary mixtures A-Kr, A-Xe, and Kr-Xe. The pressure of the component with the greater excitation potential was 7×10^{-1} mm Hg; that of the component with the smaller excitation potential was 0.8×10^{-1} mm Hg. Each mixture was studied at currents of 1.2, 0.6, and 0.3 amp. Under these conditions, intense emission of light by the ions of both components was observed. In addition, measurements of ionic mobility were carried out in pure A, Kr, and Xe for the same currents and at a pressure equal to the total pressure in the mixtures.

The measurements were made in a discharge tube 4 mm in diameter and 110 mm long. Two cylindrical probes were sealed into the central portion of the discharge tube; these were 0.2 mm in diameter and 2.5 mm long, and were spaced 4 cm apart. The spectra were studied in the direction of the axis of the positive column, through a plane window. A 2-PS spectrograph crossed with a Fabry-Perot etalon with 15 and 30 mm spacings was used; the reflecting surfaces of the latter were provided with dielectric coatings. The lines studied were A II 4806 and 4848 Å, Kr II 4832 and 4739 Å, and Xe II 5292 Å. Measurements of the displacements were made on the third and fourth rings. For each set of the experimental conditions, two exposures were made and the values of the displacements from the two plates were averaged.

Values of the drift velocities of the ions as calculated from the measured displacements of the lines are given in Table 1. Values of the longitudinal field intensity E as measured by the two probes are given in Table 2.

2. The data of Tables 1 and 2 can be used to calculate the mobility b from the relation

$$v = bE. \quad (1)$$

Equation (1) is valid only for fields which are sufficiently small for the following inequality to hold:

Table 1. Ionic Drift Velocities $v \times 10^{-4}$ (in cm/sec)

Current (amp)	A	Kr	Xe	A-Kr		A-Xe		Kr-Xe	
				A	Kr	A	Xe	Kr	Xe
1.2	1.55	0.9	0.5	1.5	1.35	1.5	1.1	1.0	0.95
0.6	1.35	0.8	0.4	1.3	1.1	1.25	1.0	0.7	0.7
0.3	1.15	0.6	—	1.1	0.9	1.0	0.85	—	—

Table 2. Longitudinal Field Strength E (in volts/cm)

Current (amp)	A	Kr	Xe	A-Kr	A-Xe	Kr-Xe
1.2	4	3.3	3	3.6	3.4	2.8
0.6	4	3.3	3	4	3.8	3.0
0.3	4.2	3.3	—	4.2	4.0	3.0

sufficiently small for the following inequality to hold:

$$\frac{eE}{kTnq} \ll 1, \quad (2)$$

where T is the temperature of the gas, n is the concentration of normal atoms, and q is the cross section for collision of the ions with the atoms of the gas.

According to the data of ref. 2, the gas temperature T for argon is approximately 10^3 °K. The concentration of normal atoms was calculated from the formula $n = p/kT$, where p is the pressure measured in the absence of a discharge. The possible occurrence of a breakdown in the tube introduces some uncertainty in the value of concentration; however, since in our case the current densities were not too great, this effect must be negligible. Under our conditions criterion (2) is then fulfilled.

Table 3 gives the values of the ionic mobilities calculated from formula (1). An examination of the data in Table 3 leads to the conclusion that the ionic mobility of the major component of the mixture is practically identical with that of the pure gas. On the other hand, the ionic mobility of a component is in general greater when it is a minor constituent than when it is the principal gas. This effect can be qualitatively explained by the fact that for the pure gas the ionic mobility is determined by char-

Table 3. Ionic Mobilities $b \times 10^{-6}$ (in $\text{cm}^2/\text{sec}/\text{cgs}$ unit of field intensity)

	A	Kr	Xe	A-Kr		A-Xe		Kr-Xe	
				A	Kr	A	Xe	Kr	Xe
0.2	1.15	0.8	0.5	1.25	1.1	1.3	1.0	1.0	1.0
0.6	1.0	0.7	0.4	1.0	0.8	1.0	0.8	0.7	0.7
0.8	0.85	0.56	—	0.8	0.65	0.75	0.65	—	—

transfer, whereas the mobility of an ion in a foreign gas is determined both by charge transfer and by polarization forces. However, the cross section for charge transfer is greater than the cross section associated with polarization forces (Langevin cross section). A certain rise in ionic mobilities with increasing current is evidently related to breakdown in the discharge gap.

It is possible to make an approximate calculation of the ionic mobilities for our experimental conditions. In weak fields, where the charge transfer mechanism predominates, the following relation holds³:

$$b_1 = 0.5 \frac{e}{qn \sqrt{3kTM}}, \quad (3)$$

where q is the cross section for charge transfer and M is the mass of the ion.

According to the data in ref. 3, the charge transfer cross sections for the ions studied here are

$$q_{Ar} = 6.5 \cdot 10^{-15}, \quad q_{Kr} = 8 \cdot 10^{-15} \text{ and } q_{Xe} = 9 \cdot 10^{-15}.$$

Calculation using formula (3) gives the following values for the ionic mobilities: 0.95×10^6 for argon, 0.52×10^6 for krypton, and 0.37×10^6 for xenon, in cm^2 per sec per cgs unit of field intensity. These results agree very well with the measured values of the ion mobilities for the case in which the charge transfer is the predominant effect.

Ionic mobility in a foreign gas is given by the Langevin formula, which for our conditions can be written in the form

$$b_2 = 0.5 \frac{\sqrt{\frac{M_a + M_i}{M_i}}}{\sqrt{(\epsilon - 1)\rho}}, \quad (4)$$

where M_a is the mass of the atom, M_i the mass of the ion, ϵ the dielectric constant, and ρ the density of the gas. For argon at 0°C and 760 mm Hg, $(\epsilon - 1) = 54.5 \times 10^{-5}$.

A direct measurement of the ionic mobilities in a mixture can be obtained from Blanc's law⁴

$$\frac{1}{b} = \frac{1}{b_1} + \frac{1}{b_2}, \quad (5)$$

where b_1 is the ionic mobility of the trace component and is associated with charge transfers of the trace atom, and b_2 is the ionic mobility of the trace component for interactions with the atoms of the main component. The ionic mobilities of krypton and xenon in A-Kr and A-Xe mixtures, calculated from formula (5), are 1.5×10^6 and 1.3×10^6 , respectively, in cm^2 per sec per cgs unit of field intensity; these agree in order of magnitude with the values measured in the present investigation.

In conclusion, the authors express their gratitude to S. E. Frish for his interest in this research and his discussion of the results.

REFERENCES

1. S. E. Frish and Yu. M. Kagan, Zhur. Eksptl. i Teoret. Fiz. 17, 577 (1947).
2. V. M. Zakharova, Opt. i Spektr. 1, 636 (1956).
3. L. A. Sena, "Stolknovenie elektronov i ionov s atomami gaza" (Collisions of Electrons and Ions with Gas Atoms). Gosudarst. Tekh. Izd., Moscow, Leningrad, 1948.
4. L. Loeb, "Osnovnye protsessy elektricheskikh razryagov v gaze" (Fundamental Processes of Electric Discharge in Gases). Gosudarst. Tekh. Izd., Moscow, Leningrad, 1960.

POLARIZATION OF THE LUMINESCENCE FROM MOLECULAR CRYSTALS β -RAY EXCITATION

V. I. Gribkov, N. D. Zhevandrov, and Sh. D. Khan-Magometova (pp. 549-550)

Received 9 November 1960

In previous studies¹⁻³ we used the polarization of the luminescence from molecular crystals to investigate crystal structure and the processes of energy migration in them. In particular, the study of polarization of the luminescence spectrum was used to discover the participation of free excitons in luminescence and to evaluate their role.

In one of our papers³ the polarization of photo- and -luminescence in stilbene crystals was compared. The polarization for the integral (not resolved into a spectrum) luminescence proved to be identical in both cases. If the polarization of the luminescence from the crystals conforms to the "oriented gas" model, i.e., if it is completely determined by the lattice structure and the orientation of molecules in it, then the above-mentioned fact that polarization is independent of the nature of the excitation would be trivial. The results of the previous work

show, however, that the "oriented gas" model is in substantial disagreement with experiment and that polarization is associated with exciton processes in the crystal.

For this reason it was of interest to study the polarization of luminescence from molecular crystals in more detail, under different kinds of excitation, and in particular to investigate the spectral dependence of the polarization. In this work the latter relationship was studied for stilbene and anthracene under β -excitation (a Sr^{90} compound with an activity of 100 mC). The measurements were made with the spectropolarimetric apparatus described in ref. 2. These experiments make extremely severe demands on the sensitivity of the apparatus. These requirements were successfully met by making maximum use of its illuminating power, accurate alignment, installing the crystal directly in the entrance slit of the monochromator, and using photomultiplier tubes with the

highest sensitivity and low thermal current. The tubes were specially selected from a large lot. The apparatus was equipped to sequentially measure the β -luminescence and photoluminescence of a particular sample at various wavelengths of the exciting light. A reliable shield and remote controls were also provided.

An abrupt change in the polarization at the short wavelength end of the spectrum from stilbene under photoexcitation, which we connected with the emission of free excitons, has already been detected.^{2,3} It should be noted that this change in polarization is much more marked with excitation by light at a wavelength of 365 m μ than with shorter wavelength excitation (313 and 254 m μ).³ Hence it can be concluded that the fraction of the emission dependent on free excitons is reduced in the latter case.

The dependence of the degree of polarization on the wavelength of the luminescence from a single crystal of stilbene under β -excitation (and for comparison under excitation by light at 313 m μ) is shown graphically in Fig. 1. The crystal slab was sawed off parallel to the ab plane. It is easy to see that under β -excitation there is no change in the polarization at the edge of the luminescence spectrum, i.e., there is practically no radiation from free excitons. However, in the long wavelength region of the spectrum the polarization is the same as in the case of photoexcitation. The measurements were made on several samples with consistently reproducible results.

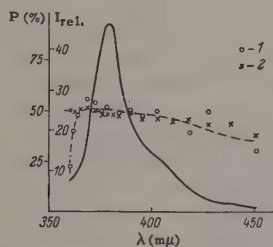


Fig. 1. The dependence of the degree of polarization on the wavelength of the luminescence for a stilbene crystal. 1—Under excitation with light with a wavelength of 313 m μ ; 2—under β -excitation. The solid curve is the luminescence spectrum. The surface of the crystal was the ab plane (the "b" axis was horizontal).

Similar data for anthracene are shown in Fig. 2. These experiments could not be conducted on the commonly used single crystal films of anthracene, which are prepared by sublimation, since the over-all thickness of such films is only a few microns and the β -luminescence excited in them is much too low in intensity. We used thin slabs which were sawed from large single crystals parallel to the ab plane. These thin slabs and also the stilbene slabs were of the order of 1 mm thick. It was pointed out in ref. 2 that in similar experiments with anthracene it is essential to take the dichroism of the crystals into account. In order to reduce the effect of dichroism an appreciable improvement can be made by exciting the crystal from the same side from which the luminescence is observed, rather than from the opposite side. However this is not experimentally practicable in the case of β -luminescence; in addition to which the polarization of β - and photoluminescence must be compared under the same conditions. In the case under consideration the difficulty is made worse by the large

thickness of the crystal and, consequently, the short wavelength region of the luminescence spectrum is appreciably distorted because of reabsorption. For this reason we only present polarization data in Fig. 2 for that portion of the luminescence spectrum in which anthracene is transparent (to approximately 415 m μ); however, a change in polarization has already taken place and in the present case we only want to compare the effect under photo- and β -excitation. It is seen from Fig. 2 that the picture is somewhat different in the case of anthracene than for stilbene. On switching from photo- to β -excitation the change in polarization at the edge of the spectrum still remains very significant although it is appreciably reduced. When the wavelength of the exciting light is changed from 365 to 313 m μ practically no deviation is observed. In other words the same effect appears much weaker in anthracene than in stilbene. The polarization in the long wavelength region of the spectrum is the same under all kinds of excitation for which the luminescence spectra do not vary as a function of the nature of the excitation.

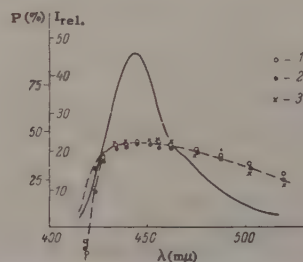


Fig. 2. The dependence of the degree of polarization on the wavelength of luminescence for an anthracene crystal. 1—Under excitation by light with a 365 m μ wavelength; 2—same for 313 m μ ; 3—under β -excitation. The solid curve is the luminescence spectrum. The surface of the crystal is the ab plane (the "b" axis is vertical).

Thus the role of free excitons in the luminescence of molecular crystals is less under β -excitation than during photoluminescence and occasionally they play no role at all. A similar relationship is observed when the wavelength of the exciting light is reduced, but this dependence manifests itself much more weakly. The following hypothesis seems to naturally connect this fact with the high probability of ionizing the molecules under β -excitation: if the subsequent recombination produces an excited molecule then there is a high probability that it will be a localized exciton state because the ionized state which is associated with substantial changes in the field of the molecule produces a severe local deformation of the surrounding lattice. Of course this hypothesis requires independent corroboration.

REFERENCES

1. N. D. Zhevandrov, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **22**, 1332 (1958).
2. N. D. Zhevandrov, V. I. Gribkov, and V. N. Varfolomeeva, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **23**, 57 (1959).
3. V. I. Gribkov, N. D. Zhevandrov, and Sh. D. Khan-Magometova, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **24**, 740 (1960).

DISSOCIATION IN SENSITIZED PHOTOCHEMICAL REACTIONS

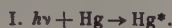
G. S. Gordadze (pp. 551-552)

Received 15 November 1960

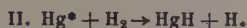
The problem of molecular dissociation resulting from the collision of molecules with the excited atoms of a sensitizer is of great theoretical interest from the point of view of elucidation of the physical nature of this phenomenon. In this communication we shall attempt a qualitative explanation of this phenomenon.

It is known¹⁻⁴ that molecular hydrogen (H_2) is transparent to light of frequency ν corresponding to the mercury line with the long wavelength $\lambda = 2537$ Å. However, the photochemical dissociation of H_2 may be realized with the help of light of the mentioned frequency ν , if one uses mercury as a sensitizer.

In the process of photochemical production of atomic hydrogen from molecular hydrogen a considerable role may be played by the atomic mercury. In the first stage of reaction (I) the atoms of the sensitizer absorb light quanta corresponding to the mercury line and are transformed into an excited state Hg^* , i.e.,



In the second stage the excited mercury atoms collide with hydrogen molecules with the following resulting reaction:



We must note that Laidler⁵ proposed a complex scheme for the production of atomic hydrogen under the influence of the sensitizer Hg , which however is not sufficiently founded from an energetic point of view.

The process of energy transfer from the Hg^* atoms to the H_2 molecules is important and interesting insofar as the energy of excitation of the Hg^* atoms is sufficient for the dissociation of the hydrogen molecule. Indeed, the mercury line $\lambda = 2537$ Å corresponds to a light quantum

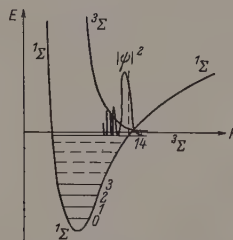
$$h\nu = 4.886 \text{ ev}, \quad (1)$$

which is very close to the dissociation energy of the hydrogen molecule:

$$D(H_2) = 4.72 \text{ ev}. \quad (2)$$

The approximate coincidence of the values (1) and (2) is obviously indispensable for the excitation of a H_2 molecule into a higher vibrational state (with the vibrational quantum number $v = 14$) and for the possibility of its dissociation with the subsequent formation of the molecule HgH and of atomic hydrogen H .

In the well-known monograph by Bongeffer and Gartek⁴ it is pointed out that "besides this (besides the dissociation of the H_2 molecule with the formation of HgH and H according to the reaction II) the possibility of the formation of strongly vibrating metastable H_2 molecules must be also taken into account." This conclusion is in agreement with our theoretical results.⁶⁻⁹ Indeed, according to these results,⁶⁻⁹ the potential curve $^1\Sigma$ of the H_2 molecule intersects the curve $^3\Sigma$ (see the diagram); i.e., for the dissociation of a H_2 molecule it is not sufficient to excite it into a higher vibrational state (with the vibrational quantum number $v = 14$). It is also necessary



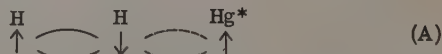
to transfer the excited hydrogen molecule (characterized by the quantum number $v = 14$) at the point of the intersection of the terms ($^1\Sigma$, $^3\Sigma$) from the state $^1\Sigma$ to the state $^3\Sigma$. This transition has a reasonable probability of occurring only when in the presence of a third atom.

A qualitative estimate of the numerical probability of this occurrence is given in our work⁹ for the case when the third atom is a hydrogen atom in its ground state and when the collision takes place via a linearly symmetrical distribution of the nuclei.

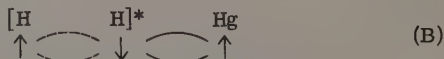
At the same time the transition $^1\Sigma \rightarrow ^3\Sigma$ is enhanced by the fact that the hydrogen atom in this system has the greatest probability of being in the vicinity of the intersection of the curves ($^1\Sigma$, $^3\Sigma$) (see the qualitative curve $|\psi|^2$ for $v = 14$ on the diagram).

This consideration points to the following scheme for the dissociation of the hydrogen molecule under the influence of the atoms of a sensitizer.

(a) In the first stage the Hg^* atom interacts with that atom of the H_2 molecule whose spin is antiparallel to the spin of the Hg^* atom. This interaction is illustrated by the scheme (A), in which the arrows under the chemical symbols indicate the direction of the spins. The symbol $\frown$ corresponds to the strong interaction whereas $\smile$ corresponds to the weak interaction.

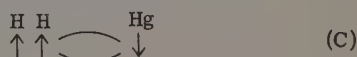


(b) In the second stage the excitation energy of the Hg atom is transferred to the H_2 molecule, while the latter is excited to the higher vibrational state (with $v = 14$). At the same time the bond between the hydrogen atoms is being weakened while the bond between the atoms Hg and H is being strengthened, which is illustrated by the scheme (B):



In spite of the weakening of the bond in the H_2 molecule, it is still not dissociated while the spins in it are antiparallel.

(c) In the last stage the change in the spin direction is taking place according to the scheme (C), and the H_2 molecule is dissociated with the transition $^1\Sigma \rightarrow ^3\Sigma$:



The probability of the above-mentioned processes,

i.e., the probability of transition from the spin configuration ($\alpha\beta\alpha$) to the configuration ($\alpha\alpha\beta$), where α is the spin function of positive spin and β that of negative spin, is according to our evaluation⁹ quite significant for the effective realization of the mechanism of photochemical dissociation of H_2 under the influence of a sensitizer.

If the hydrogen molecule absorbs a light quantum (of sufficient energy for the excitation to the vibrational level $v = 14$), but the collision with the sensitizer atom does not take place, then such a molecule, because of the intersection of the terms $^1\Sigma$ and $^3\Sigma$, can not be dissociated

insofar as the probability of transition $^1\Sigma \rightarrow ^3\Sigma$ within the H_2 molecule (without the sensitizer) is equal to zero. These molecules represent "strongly vibrating metastable molecules" H_2^* , which were mentioned in the monograph⁴ cited above. Thus, the physical explanation of the dissociation of H_2 molecules in sensitized photochemical reactions is in agreement with the theoretical results concerning the intersection of the potential curves $^1\Sigma$ and $^3\Sigma$ of the H_2 molecule which we previously obtained. The results of this work were discussed with A. V. Karyakin, to whom I express my gratitude.

REFERENCES

1. G. Cario and J. Franck, Z. Physik 11, 161 (1922); Ibid. 37, 61 (1926).
2. H. Beutler and E. Rabinovitsch, Z. physik. Chem. 8, 403 (1930).
3. H. Sentfleben, Z. Physik 33, 871 (1925).
4. K. F. Bongeffer and P. Gartek, "The Fundamentals of Photochemistry." Izd. Khim. Lit., Moscow, 1935.
5. K. J. Laidler, "The Chemical Kinetics of Excited

States," Oxford Univ. Press, 1955; "Chemical Kinetics." New York, 1950.

6. G. S. Gordadze, Trudy Gruzin. Politekh. Inst. No. 2 (37), 93, 117 (1955).
7. G. S. Gordadze, Trudy Gruzin. Politekh. Inst. No. 1 (142), 125 (1956).
8. G. S. Gordadze, Trudy-Gruzin. Politekh. Inst. No. 7 (55), 91 (1957).
9. G. S. Gordadze, Trudy Gruzin. Politekh. Inst. No. 2 (62), 139 (1958).

THE ROTATIONAL SPECTRUM OF THE CYANAMIDE MOLECULE

G. P. Shipulo (pp. 553-554)

Received 19 November 1960

The rotational spectrum of cyanamide vapors at room temperature has been investigated by the microwave method in the 20, 40, and 60 kMc regions. The character of the spectrum obtained corresponds to the molecular structure $H_2N-C\equiv N$ with C_{2v} symmetry, as determined for the solid state.¹

The measured frequency values of the absorption lines and the relative intensities within each $J \rightarrow J+1$ line group are presented in the Table. The identification of the lines was made on the basis of the Stark effect; the intensities were compared visually on the oscillograph screen.

The frequencies of the lines assigned to the ground vibrational state ($v=0$) correspond to transitions between the energy levels of an asymmetric rotor which is close to an elongated symmetrical one.² Then

$$\frac{w}{h} = \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2} \right) w(k, b) - D_J J^2 (J+1)^2 - D_{JK} J(J+1) K^2 - D_K K^4, \quad (1)$$

where

$$w(K, b) = K^2 + C_1 b + C_2 b^2, \quad b = -\frac{B-C}{2A-B-C}, \quad K = K_{-1}.$$

The following values were obtained for the rotational constants (in Mc):

$$B_0 + C_0 = 19995.8 \pm 0.2; \quad B_0 - C_0 = 264 \pm 0.3; \quad D_{IK} = 0.56 \pm 0.05; \\ D_J \approx 0.01 \text{ and } A_0 b^2 \approx 0.05.$$

The error in the computations is basically determined by the effect of the hyperfine structure resulting from the quadrupole moment of the nitrogen nucleus, which was not resolved.

The relative intensities were evaluated according to

the formula

$$\frac{\alpha_0(K)}{\alpha_0(0)} = \frac{\left[1 - \frac{K^2}{(I+1)^2} \right] g_v(K)}{g_v(0)},$$

where $g_v(K)$ is the nuclear statistical weight of the levels involved in the transition $J, K \rightarrow J+1, K$. At thermal equilibrium, the cyanamide vapors are a mixture of two modifications of the H_2NCN molecule—ortho (hydrogen spins parallel) and para (hydrogen spins antiparallel)—in the ratio 3:1. The complete wave function of the molecule is odd with respect to interchange of the H nuclei ($I = 1/2$). In the case of C_{2v} symmetry, such an interchange is accomplished by the operation C_2^x (the a axis coincides with $N-C\equiv N$), the rotational function being multiplied by $(-1)^K$. Therefore, in the ground vibrational state, the ortho modification has only rotational levels with odd K and the para modification only those with even K ; i.e., the ratio $g_o(K)/g_o(0)$ equals 3 for K odd and 1 for K even.

As can be seen from the Table, the computed values of $\alpha_0(K)/\alpha_0(0)$ agree well with those observed. For the excited vibrational state ($v=1$), the computed values of

$J \rightarrow J+1$	K	$v=0$					$v=1$				
		Frequency (Mc)	$\frac{\alpha_0(K)}{\alpha_0(0)}$		$g_o(K)$		Frequency (Mc)	$\frac{\alpha_1(K)}{\alpha_1(0)}$		$g_o(K)$	
			Experiment	Calculation				Experiment	Calculation		
0 → 1	0	19995.8 ± 0.2	1	1	1	19980.0 ± 0.2	1	1	3	2	2
	1	39991.0 ± 0.3	1	1	1	39959.4 ± 0.3	1	1	3	2	2
1 → 2	1	39725.1 ± 0.3	2	2.25	3	39713 ± 0.3	< 0.25	0.25	1	1	3
	2	40252.8 ± 0.3	2	2.25	3	40205.4 ± 0.3	< 0.25	0.25	1	1	3
2 → 3	0	59986.0 ± 0.4	1	1	1	59937.6 ± 0.4	1	1	3	2	2
	1	59586.8 ± 0.4	2.5	2.7	3	59569.6 ± 0.4	< 0.3	0.3	1	1	3
	2	60379.2 ± 0.4	2.5	2.7	3	60308.0 ± 0.4	< 0.3	0.3	1	1	3
	3	59973.0 ± 0.4	1	1.1	1	59848.8 ± 0.4	1	1.1	3	2	2

$\alpha_1(K)/\alpha_1(0)$ correspond to the experimental ones only for normal vibrations of type B, for in this case the ortho modification has only rotational levels with even K and the para modification those with odd K, and the ratio $\alpha_1(K)/\alpha_1(0)$ equals 1 for K even and 1/3 for K odd. It follows from the data presented that the lines with even K are twice as intense when $v = 1$ as when $v = 0$. Inasmuch as

$$\frac{\alpha_1(K)}{\alpha_0(K)} = \frac{g_1(K)F_1}{g_0(K)F_0},$$

where F_v is the relative population of the vibrational state, then when $\alpha_1/\alpha_0 = 2$, $F_1/F_0 = 2/3$. For the molecule H_2NCN in the case of C_{2v} symmetry, there are 5 normal vibrations of type B (3 B_1 and 2 B_2). Between vibrations of types B_1 and B_2 , when their frequency values are close together, an interaction brought about by the rotation of the molecule is possible.³ Assuming for the purposes the presence of a nearly doubly degenerate vibration (deformation vibrations of the N—C≡N group or the H₂ group), we obtain $F_1/F_0 = 2e^{-h\nu/kT} = 2/3$, whence $\nu = 230 \pm 30$ cm⁻¹ at $T = 300^\circ K$ (considering the error in the determination of the ratio α_1/α_0 to equal 25%). If we assume the excited state to be nondegenerate, then we obtain $\nu = (90 \pm 20)$ cm⁻¹. The position of the lines assigned to $v = 1$ corresponds most closely to the first assumption—the displacement of the frequencies of the $K = 1$ and $K = 2$ lines with respect to the $K = 0$ line for given $J \rightarrow J + 1$ does not correspond to expression (1) and may be produced by a rotational-vibrational inter-

action. From the frequency values of the $K = 0$ lines we have: $B + C = 19,980$ Mc and $D_J \approx 0.02$ Mc for $v = 1$.

A more detailed study of the spectrum of the H_2NCN molecule and its isotopic variants will be carried out in the future.

In communication 4, the values $B_0 + C_0 = 19,951.1 \pm 1$ Mc and $B_0 - C_0 = 263.7 \pm 0.1$ Mc are given for the molecule studied here. The substantial deviation (45 Mc) of the value of $B_0 + C_0$ from the quantity obtained in the present work may be explained by the fact that the authors⁴ observed the spectrum of a mixture of the molecules H_2NCN , D_2NCN , and $HDNCN$ and may have made an error in the identification of the lines.

REFERENCES

1. T. Davies and W. J. Jones, *Trans. Faraday Soc.* **54**, 1454 (1958); B. I. Sukhorukov and A. I. Finkel'shtein, *Opt. i Spekt.* **7**, 653 (1959), *Optics and Spectroscopy* **7**, 393 (1959).
2. C. Townes and A. Schawlow, "Radiospektroskopiya" (Microwave Spectroscopy). Izd. Inostrannoi Lit., Moscow, 1959. McGraw-Hill, New York, 1955.
3. G. Herzberg, "Molecular Spectra and Molecular Structure II" Infrared and Raman Spectra of Polyatomic Molecules. Van Nostrand, New York, 1945. Izd. Inostrannoi Lit., Moscow, 1949.
4. J. K. Tyler, L. F. Thomas, and J. Sheridan, *Proc. Chem. Soc.*, 155 (1959).

A STUDY OF THE PHOTOLUMINESCENCE AND SCINTILLATION PROPERTIES OF SOME 1, 3, 4-OXADIAZOLE DERIVATIVES IN POLYSTYRENE

L. L. Nagornaya, V. D. Bezuglyi and A. P. Grekov (pp. 555-556)

Received 21 November 1960

Aryl and functional derivatives of 1, 3, 4-oxadiazole have been studied in liquid solutions.^{1,2} A number of papers^{3,4} have reported on the use of some derivatives of this class of compounds as effective luminescing additives in plastic scintillators. For this reason we studied a large number of oxadiazole-1, 3, 4 derivatives; along with the study of aryl derivatives, derivatives of 2-(9-phenanthryl)-oxadiazole 1, 3, 4 not described in the literature were also synthesized and studied. All the compounds were studied for their capacity as luminescing additives in plastic scintillators. Measurements were made of their luminescence spectra, photoluminescence quantum yield, and scintillation efficiency.

The synthesis and refining of the materials under consideration are not described in the literature. The following method was used to obtain the phenanthryl derivatives of oxadiazole:



These materials were purified by recrystallization

from the appropriate solvents, and after that in a chromatographic column. The methods of producing and refining the rest of the materials are described in detail in ref. 5. The samples of plastic scintillator required for the study were prepared by high temperature polymerization of styrene⁶ in sealed ampoules in a nitrogen atmosphere. The specimens used for the investigation were cylindrical in shape with a diameter of 18 mm and a height of 15 mm.

The luminescence spectra were measured with an SF-4 spectrophotometer which was used as a monochromator with a special photoelectric attachment.⁷ An FEU-18 photomultiplier was used as the detector; this was calibrated with an incandescent lamp having a known color temperature with correction for passage through the glass of the tube. The photoluminescence was excited from the front by the lines with wavelengths of 313 and 334 mμ which were isolated from the spectrum of a PRK-2 quartz mercury lamp by a composite spectrofilter.⁷

The relative quantum yield values were measured under conditions of total light absorption following the

Scintillation and Optical Characteristics of 1,2,3,-oxadiazole Derivatives

No.	Luminescing additive	$\lambda_{\max}$ of absorption in heptane (m μ)	$\lambda_{\max}$ of luminescence in plastic scintillator (m μ)	B	C _{opt} (%)	I _{sc} .
1	2,5-diphenyl-oxadiazole-1,3,4	285	335	—	1.5	82
2	2-(4-biphenyl)-5-phenyl-oxadiazole-1,3,4	287	350	—	—	—
2	2-(4-biphenyl)-5-phenyl-oxadiazole-1,3,4	300	365	1.3	1.5	130
3	2-(1-naphthyl)-5-phenyl-oxadiazole-1,3,4	325	375	1.1	1.5	133
4	2-(2-naphthyl)-5-phenyl-oxadiazole-1,3,4	300	365	—	1.5	119
5	2,5-di-(4-diphenyl)-oxadiazole-1,3,4	325	370	1.4	0.8	170
6	2,5-di-(2-naphthyl)-oxadiazole-1,3,4	315	370	—	1.5	140
7	2,5-di-(1-naphthyl)-oxadiazole-1,3,4	—	390	1.1	1.5	152
8	2-(1-naphthyl)-5-(4-biphenyl)-oxadiazole-1,3,4	320	390	—	1.5	170
9	2-phenyl-5-(9-phenanthryl)-oxadiazole-1,3,4	325	400	0.46	1.5	91
10	2-(4-biphenyl)-5-(9-phenanthryl)-oxadiazole-1,3,4	—	405	0.90	1.5	145
11	2-(1-naphthyl)-5-(9-phenanthryl)-oxadiazole-1,3,4	320	405	0.66	1.5	140
12	2-(2-naphthyl)-5-(9-phenanthryl)-oxadiazole-1,3,4	248	415	—	—	—
12	2-(2-naphthyl)-5-(9-phenanthryl)-oxadiazole-1,3,4	325	400	0.95	1.5	107
13	2,5-di-(9-phenanthryl)-oxadiazole-1,3,4	250	415	—	—	—
13	2,5-di-(9-phenanthryl)-oxadiazole-1,3,4	—	405	—	low solubility	79

method described in ref. 8. A plastic scintillator with added 2,5-diphenyloxazole-1,3(PPO) ($C = 10^{-3}$ moles/liter) was used as a standard.

The scintillation efficiency was measured by variations in the photocurrent of the FEU-29 photomultiplier when the samples were exposed to an Ag^{110} gamma source. A plastic scintillator with n-terphenyl (PTP) ($C = 2\%$) as the admixed agent served as a standard for comparison. The scintillation efficiency comparisons were conducted with the luminescing materials at optimum concentrations. The proper concentrations were for the most part determined from the concentration dependences of scintillation efficiency which we had obtained and from the data of ref. 4. For the majority of the highly soluble materials $C_{\text{opt}} = 1.5\%$.

The results of the measurements are shown in the Table. It is seen from the data obtained that the introduction of a substituent with a greater number of conjugated bonds into a molecule leads to a shift in the luminescence spectrum toward the long wavelength region. The introduction of biphenyl and naphthyl groups shifts both luminescence maxima toward the long wavelength side by 30 to 40 m μ . The addition of a phenanthryl radical in the fifth position of oxadiazole is accompanied by a displacement of the first maximum by 65 to 70 m μ (relative to the 2,5-diphenyloxazole spectrum); while the second maximum is shifted 50, 65, or 76 m μ depending on whether biphenyl, naphthyl, or phenanthryl substituents respectively are introduced in the second position. Thus increasing the conjugation in the substituent displaces the luminescence spectra toward the long wavelength region. A comparison of the quantum yield values (B) of the compounds studied shows that the biphenyl derivatives have the highest B and the phenanthryl the lowest. These data do not give a well-defined answer to the question of just how the increase in the conjugation of the chains influences the quantum yield. Apparently the effect of wasting energy in radiationless paths due to vibration of the heavy groups (in our case the phenanthryl radicals) has the greater effect on the afore-mentioned property.

Of the luminescing additives that were studied in

plastic scintillators 2,5-di-(4-biphenyl)-oxadiazole-1,3,4 and 2-(1-naphthyl)-5-(4-biphenyl)-oxadiazole 1,3,4-in polystyrene are of the most interest from the point of view of scintillation efficiency, since their light yield somewhat exceeds (by about 10%) the light yield of widely used plastic scintillators with n-terphenyl and 1,4-di-(2-(5-phenyl)-oxazolyl)-benzene (POPOP) additives. They combine well with polystyrene up to a concentration of 0.8-1% and are stable at a temperature of 200°. They can therefore be recommended as luminescing additives for production of plastic scintillators suitable for use in combination with photomultiplier tubes having maximum spectral sensitivity near 4000 Å. Lifetimes (τ_{fl}) of $2.2 \sim 3 \times 10^{-9}$ sec were measured for the excited states of plastic scintillators with these additives.*

*The value τ_{fl} was measured on a GOI fluorimeter, and the authors express their thanks to B. Ya. Sveshnikov and his co-workers for conducting the measurements.

The data on the phenanthryl derivatives which have a high I_{sc} value and a relatively low quantum yield is particularly interesting. The somewhat higher values of scintillation efficiency for the plastic scintillators with phenanthryl derivatives, in comparison with the corresponding aryls, can apparently be explained by the better matching of the luminescence spectrum of the phenanthryl derivatives to the spectral sensitivity of the photomultiplier tube used for the measurements.

Thus the scintillation effectiveness of luminors is determined not only by their quantum yield values but, as it has been repeatedly pointed out previously, also by the position of the luminescence spectra with respect to the spectral sensitivity curve of the photon detector. It should also be kept in mind that in addition to the factors mentioned, the transparency of the plastic scintillator with respect to its own radiation, as well as the mechanism of the energy transfer from the excited molecules of the host material to the luminescing additive with a given concentration, have a great influence on the scintillation efficiency.

REFERENCES

- N. Hayes, D. Ott, and V. Kerr, *Nucleonics* **13**, 38 (1955).
- O. P. Shvaika and A. P. Grekov, *Opt. i Spekr.* **7**, 824 (1959), *Optics and Spectroscopy* **7**, 483 (1959).
- N. A. Adrova, M. M. Koton, Yu. N. Panov, and F. S. Florinskii, *Pribory i Tekh. Ekspt.* No. 3, 43 (1957).
- N. P. Shimanskaya, A. P. Klimov and A. P. Grekov, *Opt. i Spekr.* **8**, 194 (1959), *Optics and Spectroscopy* **6**, 124 (1959).
- A. P. Grekov and R. S. Azen, *Zhur. Obshchei Khim.* **29**, 1995 (1959).
- E. A. Andreeshchev, E. E. Baroni, K. A. Kovyrzina, I. E. Pani, I. M. Rozman, and V. M. Shoniya, *Pribory i Tekh. Ekspt.* No. 1, 32 (1956).
- A. P. Kilimov, L. L. Nagornaya, and B. A. Zadorozhnyi, *Pribory i Tekh. Ekspt.* No. 3, 105 (1959).
- A. S. Cherkasov, G. A. Tishchenko, and K. G. Voldaikina, *Opt. i Spekr.* **4**, 344 (1958).

THE LUMINESCENCE SPECTRA AND SCINTILLATION PROPERTIES OF PARA-MONOHALOGEN SUBSTITUTED TRANS-STILBENE

L. Ya. Malkes, L. L. Nagornaya, and A. I. Timchenko (pp. 557-558)

Received 21 November 1960

Various diaryl-substituted ethylenes are now widely used as scintillation materials.

There are numerous methods of using these substances as scintillators; for example, single crystals¹ are grown from them, they are used as primary or secondary additives in mixed single crystals,² plastics,³ etc. Although the diaryl-substituted ethylenes have high scintillation efficiency in single crystals and plastics, they have low efficiency in toluene solutions.⁴ The latter fact is apparently due to a photochemical change in the trans-form. The probability of such a change is negligible in solid solutions because of the high probability of radiative transitions.

During an investigation of the effects of functional groups on scintillation properties, we discovered that the introduction of chlorine into stilbene molecules in the para position led to a 1.5-fold increase in the scintillation efficiency of polystyrene blocks⁵ (in comparison with the addition of stilbene). A series of para-monohalogen substituted trans-stilbenes was synthesized for the purpose of studying the effects of the various substituents on the scintillation and luminescence properties.

4-fluorostilbene was made by thermal decomposition of stilbene diazonium fluoborate (m. p. 126°C), and 4-chlorostilbene by combining diazotized 4-chloraniline with styrene (m. p. 130°C). 4-bromostilbene was synthesized from a diazotized hydrochloric salt of 4-amino-stilbene and a solution of cuprous bromide (m. p. 135°C), and 4-iodostilbene was obtained from 4-iodobenzaldehyde and benzyl chloride (m. p. 152°C). The stilbene was synthesized by thermal decomposition of benzalazine (m. p. 125°C). All of the substances mentioned were recrystallized two or three times from different solvents (benzene, acetone, ethyl alcohol, pyridine, petroleum ether) and after that were passed through a chromatographic column filled with activated aluminum oxide.

The spectra and relative intensities of photoluminescence were measured for all of the materials synthesized. The measurements were made on a specially equipped F-4 spectrophotometer.⁶ The integral light output was measured by observing the magnitude of the photocurrent from an FEU-19 photomultiplier tube. A 0.1 mC Ag¹¹⁰ standard was used as a source of excitation. The scintillation efficiency measurements were made with each material at its optimum concentration in toluene.

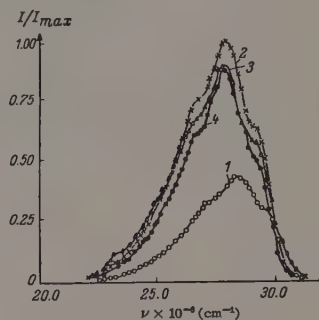
The principal results of the measurements are shown in the Table. It is easy to see that the introduction of a halogen into a stilbene molecule in the para-position has little influence on the location of the absorption and luminescence bands.

The Scintillation and Luminescence Properties of Para-Monohalogen Substituted Trans-Stilbene

No.	Material	$\nu_{\max}$, luminescence (cm^{-1})			$\nu_{\max}$, absorption (cm^{-1})	$C_{\text{opt.}}$ (gr/liter)	$I_{\text{sc.}}$ (%)
		Powder	Solution in toluene	Solution in heptane			
1	4-fluorostilbene	23100 24250 25250	26600	28350	31700	3.0	106.0
2	4-chlorostilbene	25250 26600	26600	28350	33600	3.0	145.0
3	4-bromostilbene	25400 26300	26600	28200	33500	3.0	109.0
4	4-iodostilbene	25100 25600	—	27850	31500 31400	3.0	29.0
5	stilbene	25150 26300	28400	28800	32400	5.6	100.0

Note: The scintillation efficiency of stilbene in toluene is 10% as compared with a solution of *n*-terphenyl (at optimum concentration).

Apparently, such an effect is to be expected when the weak inductive effect of halogens on the π -electron system of stilbene is taken into consideration. Typical luminescence spectra of the halogen-substituted stilbenes in toluene are shown in the Figure, which shows that the



The luminescence spectra of the materials studied in toluene solutions. Curve 1—Stilbene; curve 2—4-chlorostilbene; curve 3—4-fluorostilbene; curve 4—4-bromostilbene.

introduction of a halogen produces only an insignificant shift in the emission band maxima. Iodostilbene has such a negligible luminescence yield that it could not be compared with the other halogen derivatives. The emission bands of the crystalline materials are displaced 2000-3000 cm^{-1} to the red as compared to the solutions.

Stilbene itself is a weak scintillator in liquid solutions. As it is seen from the Table, the introduction of a halogen in the para-position leaves its scintillation properties es-

entially unchanged. All that is observed is an increase in the light yield of the chlorine derivative and a sharp reduction in scintillation efficiency when iodine is introduced into the stilbene molecule. This latter fact is apparently related to the usual quenching action of iodine. It should also be noted that the solutions of 4-iodostilbene, which have considerably smaller relative photoluminescent energy yields, also have the lowest scintillation efficiencies.

REFERENCES

1. R. S. Sangster and J. W. Irvine, *J. Chem. Phys.* **24**, 670 (1956).
2. Yu. V. Naboikin, V. K. Dobrokhotova and V. V. Uglova, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **24**, 744 (1960).
3. D. G. Ott, T. Hayes, J. E. Hammel, and J. F. Kepharet, *Nucleonics* **13**, 5 (1955).
4. H. Gilman, E. A. Weipert, J. J. Dieterich, and F. N. Hayes, *J. Org. Chem.* **23**, 361 (1958).
5. L. L. Nagornaya, A. P. Kilimov, L. Ya. Malkes, L. V. Shubina, and A. I. Timchenko, *Pribery i Tekh. Ekspt.* No. 1, 36 (1960).
6. A. P. Kilimov, L. L. Nagornaya, and B. A. Zadorozhny, *Pribery i Tekh. Ekspt.* No. 3, 105 (1959).

ON THE QUESTION OF THE NATURE OF THE ELECTRONIC STATES OF BIANTHRONE IN THE PHENOMENA OF THERMOCHROMY AND PHOTOCHROMY

V. P. Klochkov (pp. 559-561)

Received 28 November 1960

The phenomena of thermochromy and photochromy of bianthrone solutions, i.e., the phenomena of reversible color change on changing the temperature or on exposure to short-wave radiation (wavelengths less than 4500 Å), are associated with a change in the spatial configuration of the molecule.¹⁻³ The color change of a bianthrone solution is produced by the appearance of a new absorption band with a maximum around 6700 Å. The appearance of this band is explained by absorption in a new set of electronic levels, corresponding to a new nuclear configuration of the bianthrone molecule which this molecule acquires on elevation of the temperature or after exposure. It has been established by spectroscopic and crystallographic studies^{1,4} that in the normal state, A, the halves of the bianthrone molecule are bent in opposite directions along the O—O line and possibly are displaced relative to one another in the vertical plane. With regard to the states which appear in the phenomena of thermochromy (B) and photochromy (C) (Fig. 1), there is no uniform opinion either on the question of the spatial structure of the bianthrone molecule in these states, or on the question of their nature.

Hirshberg and Fischer^{5,6} and Wassermann and Davis⁷ consider that the B and C states are identical, while according to the opinion of Kortüm and Theilacker

and their collaborators^{2,3,8,9} these states have different natures (here it is supposed that bianthrone in the C state is a diradical (Doppelradical) with planar halves rotated by 90° with respect to each other). The published spectroscopic data do not allow one to decide whose point of view is correct.

Since bianthrone molecules in the C state possess paramagnetic properties,⁸ magnetic measurements could make a substantial contribution to the solution of the question. Measurements of this sort have been performed, but the results obtained in different works do not agree among themselves. Nielsen and Franke¹⁰ found that the concentration of substance in the paramagnetic state increases with an increase in temperature, i.e., the B state is paramagnetic. This fact agrees with the opinion of Hirshberg and Fischer concerning the identity of the B and C forms. However, the careful quantitative studies carried out in refs. 11 and 12 on the paramagnetic absorption of 3-carbomethoxybianthrone (which, like bianthrone, possesses thermo- and photochromic properties, but is more stable toward decomposition) have shown that the content of the paramagnetic form equals ~0.5% at 21°C and 1.6% at 210°C, while the content of the B form determined by the spectroscopic method amounts to ~2 and 10% respectively, i.e., the result obtained indicates a different nature for the B and C states.

Analysis of the results of the measurements of Nielsen and Franke shows that paramagnetic absorption of bianthrone is observed at high temperatures. At the same time, it is well known that bianthrone is quite unstable and is inclined to chemical transformations. This allows us to suppose that the results of Nielsen and Franke are associated with chemical transformations of bianthrone at high temperatures, although the authors note the absence of direct indications of decomposition of the substance.

To check this supposition, we have investigated the

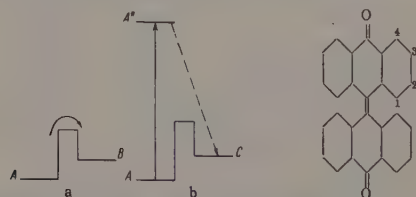


Fig. 1. Scheme of transitions in the phenomena of thermochromy (a) and photochromy (b).

temperature dependence of the intense absorption band, with a maximum around 3900 Å, of a solution of bianthrone in diethyl phthalate (solution concentration 5.8×10^{-5} moles/liter). The results of the measurements are represented in the Table and in Fig. 2, where the values of the extinction coefficient ϵ_v are given by the ordinate axis.

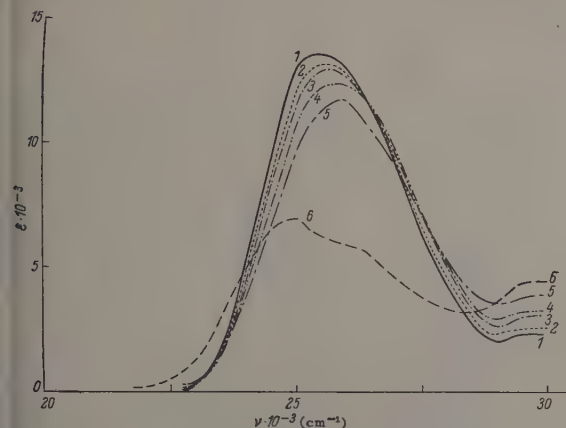


Fig. 2. Absorption spectra of solutions of bianthrone in diethyl phthalate at various temperatures. Temperature (°C): curve 1—16; curve 2—43; curve 3—74; curve 4—98; curve 5—134; curve 6—180.

In the calculation of the quantity ϵ_v , the change in solvent volume on heating has been taken into account. The oscillator strength values presented in the Table were computed according to the formula¹³

$$f = 1.3 \cdot 10^{-8} \frac{9n}{(n^2 + 2)^2} \int \epsilon_v d\nu,$$

where n is the refractive index of the solvent.

t (°C)	f
16	0.44
43	0.45
74	0.45
98	0.45
134	0.44
180	0.31

It can be seen from the Table that, on heating to a temperature of 140°C, the oscillator strength does not change within the limits of error of the experiment. Elevation of the temperature to 180° leads to an abrupt decrease in the magnitude of the oscillator strength. Analogous regularities are also observed in measurements of the shape and position of the absorption band (Fig. 2). Elevation of the temperature to 140° is accompanied by broadening of the band and by a shift to shorter wavelengths, as usually takes place in the case of spectra of organic compounds. At temperatures above 140°, an abrupt and only partially reversible change in

band shape is observed, which indicates chemical transformations of the bianthrone. At the same time, no substantial changes take place in the behavior of the long wavelength band (6700 Å).

It should be noted that the transformations just described take place most markedly in the temperature interval in which the principal paramagnetic absorption measurements of Nielsen and Fraenkel were carried out (140–200°C). The presence of an isobestic point can be seen in Fig. 2, indicating the existence of two forms of bianthrone in the solution—the spectral curves intersect fairly sharply in one point up to a temperature of 98°C. On heating to 134°C, significant changes in the spectrum are still not observed, but the corresponding spectral curve does not intersect the others at the isobestic point. This fact indicates that chemical transformations begin even at this temperature. The rate of such transformations increases rapidly with an increase in temperature.

The results obtained by us compel us to suppose that a chemical transformation product of bianthrone possesses paramagnetic absorption in Nielsen and Fraenkel's experiments. Consequently, preference should be given at the present time to the ideas of Kortüm and his collaborators,^{3,8} according to which the paramagnetic C form is a diradical (but not a triplet state) with planar halves rotated by 90° relative to one another, and the diamagnetic B form is a state in which the planar halves of the molecule are rotated relative to one another by only a small angle.

In conclusion, I thank B. S. Neporent for proposing this subject and for his sustained interest in the work.

REFERENCES

1. G. Kortüm, W. Theilacker, H. Zeininger, and H. Elliehausen, *Chem. Ber.* **86**, 294 (1953).
2. G. Kortüm, W. Theilacker, and V. Braun, *Z. physik. Chem. (N. F.)* **2**, 179 (1954).
3. G. Kortüm, *Angew. Chem.* **70**, 14 (1958).
4. E. Harnik, F. H. Herbststein, and G. M. J. Schmidt, *Nature* **168**, 158 (1951).
5. Y. Hirshberg and E. Fischer, *J. Chem. Soc.* 629 (1953).
6. Y. Hirshberg and E. Fischer, *J. Chem. Phys.* **23**, 1723 (1955).
7. E. Wassermann and R. E. Davis, *J. Chem. Phys.* **30**, 1367 (1959).
8. G. Kortüm, G. Littmann, and W. Theilacker, *Z. Naturforsch.* **12a**, 401 (1957).
9. G. Kortüm, W. Theilacker, and V. Braun, *J. Chem. Phys.* **23**, 1723 (1955).
10. W. G. Nielsen and G. K. Fraenkel, *J. Chem. Phys.* **21**, 1619 (1953).
11. W. Theilacker, G. Kortüm, and H. Elliehausen, *Z. Naturforsch.* **9b**, 167 (1954).
12. W. Theilacker, G. Kortüm, H. Elliehausen, and H. Wilski, *Chem. Ber.* **89**, 1578 (1956).
13. B. S. Neporent and N. G. Bakhshiev, *Opt. i Spekt.* **5**, 634 (1958).

TIME-RESOLVED EMISSION SPECTRA OF A SPARK DISCHARGE IN NITROGEN AND IN AIR IN THE WAVELENGTH RANGE 5000-10000 Å

M. P. Vanyukov, V. R. Muratov and I. A. Mukhitdinova (pp. 561-563)

Received 3 December 1960

In refs. 1 and 2 the time-resolved spectra of a spark discharge in inert gases were investigated in the wavelength range from 2500 to 10000 Å and were obtained by a photographic procedure.^{3,4} The time-resolved emission spectra in air at atmospheric pressure are also of considerable interest because this discharge represents the simplest impulse light source. Moreover, the spark discharge in air is often investigated in the study of the physical processes which take place in the discharge channel. A study of the time-resolved spectrum of nitrogen appears also to be useful, because the latter constitutes a basic part of the air composition.

In the present communication the results are given of the spectral intensity of light of a spark discharge in air (Fig. 1) and in nitrogen (Fig. 2) in the visible and in the infrared spectral regions. The oscillograms of light flashes for the same wavelengths are also given. The discharge in air and in nitrogen was produced at atmospheric pressure with the same parameters of the discharge circuit. The electrode gap was larger for the dis-

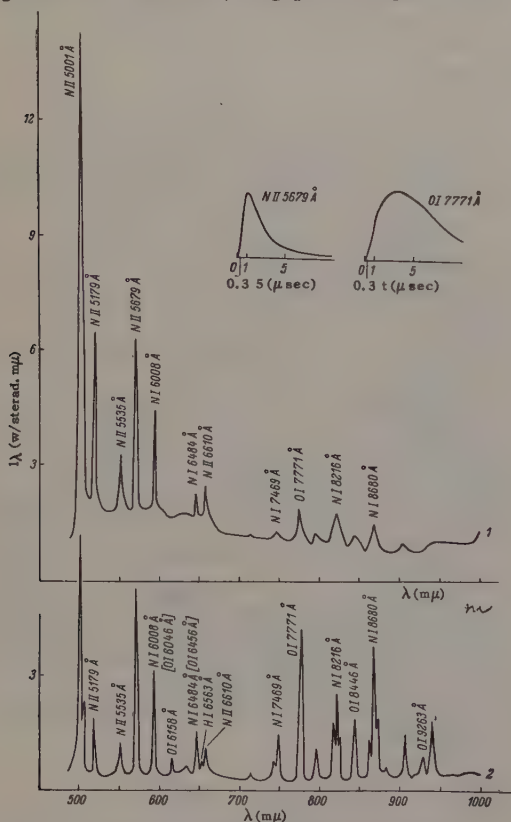


Fig. 1. Spectral light intensity of a spark discharge in air. Parameters of the discharge circuit: $P = 1$ atm; $C = 0.05 \mu\text{f}$; $V = 12$ kv; $L = 0.2 \mu\text{h}$; $l = 10$ mm; t (in μ sec): curve 1-0.3; curve 2-1.0.

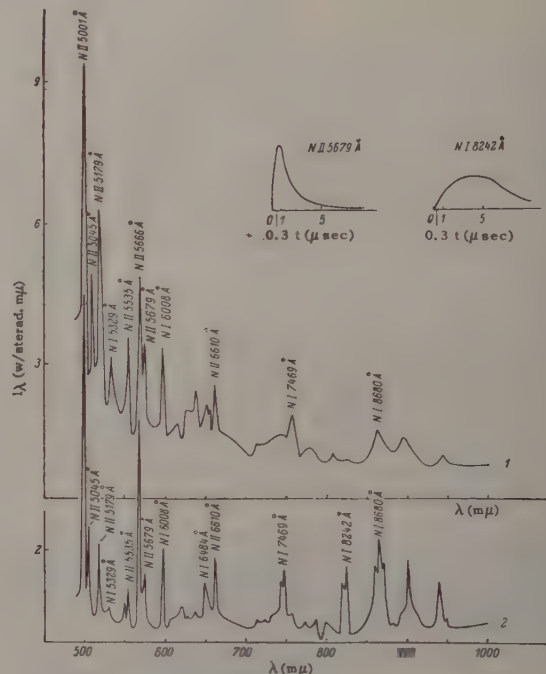


Fig. 2. Spectral light intensity of a spark discharge in nitrogen. Parameters of the discharge circuit: $P = 1$ atm; $C = 0.65 \mu\text{h}$; $V = 12$ kv; $L = 0.2 \mu\text{h}$; $l = 6$ mm; t (in μ sec): curve 1-0.3; curve 2-1.0.

charge in air than for that in nitrogen. This was caused by the necessity to maintain the same operating voltage in the study of flashes in both gases.

The comparison of diagrams in both figures shows that the air spectrum is practically identical with the nitrogen spectrum, at the discharge conditions used, and differs from the latter by the presence of several arc lines of oxygen. An increase in the self-induction of the discharge circuit to about $50 \mu\text{h}$ causes a general decrease of the spectrum intensity whereas the continuous spectrum is practically absent.

REFERENCES

1. M. P. Vanyukov, A. A. Mak, and V. R. Muratov, Opt. i Spekt. 6, 17 (1959), Optics and Spectroscopy 6, 8 (1959).
2. M. P. Vanyukov, A. A. Mak, and V. R. Muratov, Opt. i Spekt. 8, 439 (1960), Optics and Spectroscopy 8, 233 (1960).
3. M. P. Vanyukov and L. D. Khasov, Doklady Akad. Nauk 92, 523 (1953).
4. M. P. Vanyukov, B. A. Ermakov, A. A. Mak, and V. R. Muratov, Vestnik Leningrad. Univ., Ser. Fiz. i Khim. No. 16, issue 3, 25 (1959).

ON THE INTERPRETATION OF THE INFRARED SPECTRA OF THE B_2O_3 AND B_2S_3 MOLECULES

A. A. Mal'tsev and V. M. Tatevskii (p. 564)

Received 12 December 1960

The infrared spectra (principally the emission spectra) of the B_2O_3 and B_2S_3 molecules have lately been investigated by a number of authors.¹⁻⁶ A band around 2040 cm^{-1} , assigned to a stretching vibration of the B=O bond, has been observed in the emission¹⁻³ and absorption⁴ spectra of boric anhydride vapors. Aside from this band, bands at 1302 and 742 cm^{-1} , which were assigned respectively to a stretching vibration of the B—O bond and to the bending vibration of the O—B—O group, have been observed in the emission spectrum.^{2,3} Along with their studies of the infrared spectrum, the authors of ref. 3 performed a calculation of the vibrational spectrum and force constants in the angular model of the B_2O_3 molecule, starting from the three experimental frequency values, which they assigned to the antisymmetric planar vibrations of type B_1 .

We had previously carried out a calculation of the vibrational spectrum of the angular model of B_2O_3 ; no frequency value close to 1302 cm^{-1} was obtained, even on variation of the force constants within quite wide limits.

We have therefore carefully checked our results* and

to be published later.

As in the case of ref. 3 once again and have established that there is an error in ref. 3, in that one cannot obtain reasonable values for the force constants from the experimental frequency values adopted in that work and, on the other hand, one cannot obtain the frequencies of the corresponding bands from the force constant values presented by the authors.

The calculations carried out by us show that the band corresponding to the stretching vibration of the B—O group must lie in the 900 cm^{-1} region. As for the experimentally observed emission bands around 1302 and 742 cm^{-1} , they are to be considered, in our opinion, as emission or reflection bands of liquid boric anhydride, which possesses a different structure⁷ from the vapor. This conclusion is based on the coincidence of these bands with the 1316 and 720 cm^{-1} bands of the infrared reflec-

tion spectrum of liquid boric anhydride⁸ (no one has yet investigated the absorption spectrum), and also on the fact that, while the emission spectra were being obtained, as the authors themselves point out,³ a mist was observed in the cell, consisting of fine particles of the condensed phase; these could also have given a spectrum which was incorrectly assigned to gaseous B_2O_3 . It should be remarked that the contour of the 1316 cm^{-1} reflection band has a shoulder around 1400 cm^{-1} , which coincides with the position of the weak bands observed in this region in ref. 3.

A similar error in band assignment was also made for the B_2S_3 molecule.⁶ The band corresponding to the B—S stretching vibration, as our calculations have shown, must be located in the 450 cm^{-1} region, and consequently the 993 cm^{-1} band is apparently a band produced by the BS_3 group in the condensed phase.

REFERENCES

1. D. A. Dows and R. F. Porter, J. Am. Chem. Soc. **78**, 5165 (1956).
2. D. White, P. N. Walsh, and D. E. Mann, J. Chem. Phys. **28**, 508 (1958).
3. D. White, D. E. Mann, P. N. Walsh, and A. Sommer, J. Chem. Phys. **32**, 481 (1960).
4. A. A. Mal'tsev, V. K. Matveev, and V. M. Tatevskii, Doklady Akad. Nauk SSSR **137**, No. 1 (1961), Soviet Phys.-Doklady in press.
5. F. T. Greene and J. L. Margrave, J. Am. Chem. Soc. **81**, 5555 (1959).
6. A. Sommer, P. N. Walsh, and D. White, J. Chem. Phys. **33**, 296 (1960).
7. A. H. Silver and P. J. Bray, J. Chem. Phys. **29**, 984 (1958).
8. E. P. Markin and N. N. Sobolev, Izvest. Akad. Nauk SSSR, Ser. Fiz. **23**, 62 (1959).

IMPORTANT NOTICE TO ALL READERS OF OPTICS AND SPECTROSCOPY

OiS CLUB SCHEME

The Optical Society of America has been translating Optika i Spektroskopiya and distributing this monthly journal free - thanks to an NSF grant - to all OSA members and subscribers to the Journal of the Optical Society of America. This free distribution was an experiment for three years, so that the individual reader might become accustomed to reading a translation journal not as an oddity but as a publication that is looked for each month in the same manner as is J. Chem. Phys., J. Am. Chem. Soc., etc. In December of this year the NSF grant ends, but the interest in Optics and Spectroscopy is now too lively for OSA to discontinue the translation, so they have evolved the OiS CLUB SCHEME.

Put simply, this is a special subscription rate for members of those societies who wish to take part in the OiS CLUB SCHEME, viz:

To OSA members -----	\$ 7.50
To members of the OiS Club -----	\$11.00
To non-members -----	\$15.00

OSA is emphatic that if a translation journal is to be of real use (as is the case with any scientific journal) it should be read widely by all the people working in the field, and that these research results should be made available in the shortest possible time. OPTICS AND SPECTROSCOPY is published in English translation within three months of the Russian edition coming out e.g. the March 1961 issue will be published in English on June 10th. OSA is making this special offer to members of some sixty scientific societies across the English speaking world, and it asks the members of those Societies to write to their Society or directly to the Assistant Secretary, OSA, 1155 16th St., N.W., Washington 6, D.C. for further details or to send in their order. (see below)

ALL SUBSCRIBERS PLEASE NOTE that your subscriptions will start with the January 1962 issue which is published in English in March/April 1962 -- so don't start worrying when the January 1962 issue does not appear in that month!

ORDER FORM

To: OPTICS AND SPECTROSCOPY
Optical Society of America
1155 Sixteenth St., N.W.
Washington 6, D.C.

Please enter my/our subscription to OPTICS AND SPECTROSCOPY for one year commencing with the January 1962 issue (which will be published in April), at:

☐	<u>Special OSA member rate</u>	\$ 7.50
☐	<u>Special rate to members of Societies cooperating in OiS Club Scheme</u>	\$11.00

Name of your Society _____

☐ Non-members \$15.00

☐ Please send OSA membership information

Name _____

Membership no. _____

Address _____

FILLER MATERIAL - NO

IN RUSSIAN ORIGINAL

APPLIED OPTICS

to be published by The Optical Society of America

Editor: JOHN N. HOWARD, *Geophysics Research Directorate, Bedford, Mass.*

APPLIED OPTICS will publish in the areas of applied optics and closely related scientific and technical fields, e.g. physical, electron, ion, ultraviolet and space optics, lens design and optical formulas, plasma, solid state and crystal optics. **APPLIED OPTICS** will be issued bimonthly from January 1962 and will feature

..... A leader review paper on one of the major aspects of optics or its applications, e.g., new infrared detectors, new optical materials, applications of physical optics in manufacturing process control. This review will be about 10,000 words long and will set the **feature** subject of each issue.

..... Contributed technical papers—3000/5000 words each—about ten per issue—in **any area** of applied optics.

Shop and technical notes

Reports of Meetings

Government

Book reviews

Personalia

Optical Activities in

The Universities

Letters to the Editor

Meetings Calendar

Industry

Each issue will feature one area of applied optics, which feature will be the responsibility of a Subject Editor.

1962	JANUARY	— OPTICAL PUMPING AND MASERS	BRUCE H. BILLINGS
	MARCH	— SPACE OPTICS	LLOYD G. MUNDIE
	MAY	— FOREIGN OPTICS	DAVID Z. ROBINSON
	JULY	— OPTICAL ENGINEERING	RODERIC M. SCOTT
	SEPTEMBER	— INFRARED	JOHN N. HOWARD
	NOVEMBER	— INFORMATION THEORY	F. DOW SMITH
1963	JANUARY	— ASTRONOMY	JAMES G. BAKER
	MARCH	— INSTRUMENTATION	W. L. HYDE
	MAY	— INTERFEROMETRY	R. A. WOODSON

APPLIED OPTICS will be the one publication devoted solely to applied optics in its broadest sense and designed to meet the interests of scientists, engineers, technologists, technicians—in a word, opticians—working in optics or its applications, in fields borderline to optics and employing optical techniques.

Special prepublication rates for founder subscribers

All orders for a three year period, placed prior to publication, will be entered at the following special rate:

O.S.A. members—3 yr. sub. \$15.00

Non-members—3 yr. sub. \$25.00

Yearly subscription rates will be

O.S.A. members—\$6.00

Other AIP Societies members—\$8.00

Non-members—\$10.00

Subscriptions and inquiries should be sent to

Optical Society of America

1155 Sixteenth Street, N.W., Washington 6, D.C.

- Doklady Akad. Nauk SSSR - Proceedings of the Academy of Sciences of the USSR
- Izvest. Akad. Nauk SSSR - Bulletin of the Academy of Sciences of the USSR
Ser. Fiz. - Physical Series
Ser. Mat. - Mathematical Series
Otdel Khim. Nauk - Chemical Sciences Section
- Uspekhi Fiz. Nauk - Advances in Physical Sciences
- Uspekhi Khim. - Advances in Chemistry
- Zhur. Eksptl. i Teoret. Fiz. - Journal of Experimental and Theoretical Physics
- Zhur. Tekh. Fiz. - Journal of Technical Physics
- Zhur. Obshchei Khim. - Journal of General Chemistry
- Zhur. Priklad. Khim. - Journal of Applied Chemistry
- Zhur. Russ. Fiz.-Khim. Obshchestva - Journal of the Russian Physical-Chemical Society
- Zhur. Fiz. Khim. - Journal of Physical Society
- Trudy Fiz. Inst., Akad. Nauk SSSR, Fiz. Inst. im. P.N. Lebedev - Transactions of the Institute of Physics, Academy of Sciences of the USSR, named for P.N. Lebedev
- Trudy Fiz.-Tekh. Inst., Akad. Nauk Uzbek. SSR - Transactions of the Physico-Technical Institute, Academy of Sciences of the Uzbek SSR
- Trudy Inst. Krist., Akad. Nauk SSSR - Transactions of the Institute of Crystallography, Academy of Sciences of the USSR
- Trudy Inst. Nefti, Akad. Nauk SSSR - Transactions of the Petroleum Institute, Academy of Sciences of the USSR
- Trudy Gosudarst. Opt. Inst., Leningrad - Transactions of the Optical Institute in Leningrad
- Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR - Transactions of the Institute of Physics and Astronomy, Academy of Sciences of the Estonian SSR
- Trudy Inst. Fiz., Akad. Nauk Ukr. SSR - Transactions of the Institute of Physics, Academy of Sciences of the Ukrainian SSR
- Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol. - Transactions of the All-Union Scientific Research Institute of Meteorology
- Vestnik Leningrad. Univ. - Bulletin of the Leningrad University
Ser. Fiz. i Khim. - Series on Physics and Chemistry
- Gosudarst. Opt. Inst. - State Optical Institute
- Moskov. Fiz.-Tekh. Inst. - Moscow Physico-Technical Institute
- Izd. Inostrannoi Lit. - Publishers of Foreign Literature
- Izd. Akad. Nauk SSSR - Academy of Sciences Press
- Vestnik Moskov. Univ. - Bulletin of Moscow University
Ser. Fiz.-Mat. i Estestven. Nauk - Series of Physical-Mathematical and Natural Sciences
- Uchenye Zapiski Leningrad. Gosudarst. Univ. im. A. A. Zhdanov - Scientific Reports of the Leningrad State University named for A. A. Zhdanov
Ser. Fiz. Nauk - Series on the Physical Sciences
Ser. Khim. Nauk - Series on the Chemical Sciences
- Uchenye Zapiski, Moskov. Gosudarst. Univ. im. M. V. Lomonosova - Scientific Reports, M.V. Lomonosov Moscow State University
- Uchenye Zapiski Tomsk. Gosudarst. Univ. in. V. V. Kuibysheva - Scientific Reports of the Tomsk State University named for V. V. Kuibyshev
- Opt. i Spekt. - Optics and Spectroscopy
- Pribory i Tekh. Ekspt. - Instruments and Technique of Experiment
- Astron. Zhur. - Astronomical Journal
- Fiz. Metal. i Metalloved., Akad. Nauk SSSR, Ural. Filial - Physics of Metal and Metallography, Academy of Sciences of the USSR, Ural Branch
- Priboirostroenie - Instrument Manufacturing
- Zavodskaya Lab. - Factory Laboratory
- Radiotekhnika - Radio Engineering
- Radiotekh. i Elektron. - Radio Engineering and Electronics
- Inzhener.-Fiz. Zhur., Akad. Nauk Belorus. SSR - Engineering-Physics Journal, Academy of Sciences of White Russian SSR
- Ukrain. Fiz. Zhur. - Ukrainian Physics Journal
- Automat. i Telemekh. - Automatics and Telemechanics
- Nauch.-Issledovatel. Fiz.-Tekh. Inst., Leningrad. Univ. - Scientific Research Institute of Physics and Technology, Leningrad University
- Nauch.-Issledovatel. Radio-fiz. Inst., Gor'kii Univ. - Scientific Research Institute of Radiophysics, Gorki University
- Gorkov. Issledovatel. Fiz. Tekh. Inst. - Gorki Research Institute of Physics and Technology
- Gosudarst. Izd. Tekh.-Teoret. Lit. - State Publishers of Technical-Theoretical Literature
- Gosudarst. Izd. Fiz.-Mat. Lit. - State Publishers of Physical-Mathematical Literature
- Inst. Fiz., Akad. Nauk Ukr. SSR, Kiev - Institute of Physics, Academy of Sciences of the Ukrainian SSR, Kiev
- Inst. Fiz. i Astron., Akad. Nauk Eston. SSR, Tartu - Institute of Physics and Astronomy, Academy of Sciences of the Estonian SSR, Tartu

***These abbreviations must be used by Ois translators in their translations. This list will be added to from time to time.

Dissociation in Sensitized Photochemical Reactions	G. S. Gordadze	287	(551)
The Rotational Spectrum of the Cyanide Molecule	G. P. Shipulo	288	(553)
A Study of the Photoluminescence and Scintillation Properties of Some 1,3,4-Oxadiazole Derivatives in Polystyrene	L. L. Nagornaya, V. D. Bezuglyi and A. P. Grekov	289	(555)
The Luminescence Spectra and Scintillation Properties of Para-Monohalogen Substituted Trans-Stil- bene	L. Ya. Malkes, L. L. Nagornaya, and A. I. Timchenko	291	(557)
On the Question of the Nature of the Electronic States of Bianthrone in the Phenomena of Thermo- chromy and Photochromy	V. P. Klochkov	292	(559)
Time-Resolved Emission Spectra of a Spark Discharge in Nitrogen and in Air in the Wavelength Range 5000-10000 Å	M. P. Vanyukov, V. R. Muratov and I. A. Mukhitdinova	294	(561)
On the Interpretation of the Infrared Spectra of the B ₂ O ₃ and B ₂ S ₃ Molecules	A. A. Mal'tsev and V. M. Tatevskii	295	(564)

EDITOR'S NOTE

Comments on the scientific content of the translated Russian articles published in OPTICS AND SPECTROSCOPY are invited. They should be addressed as a Letter to the Editor of the Journal of the Optical Society of America and forwarded to the Editor of that journal, Dr. D. B. Judd, National Bureau of Standards, Washington 25, D. C.

CONTENTS

(Numbers in parentheses are original Russian page numbers.
These Russian page numbers are also quoted at the head of each paper.)

Oscillator Strengths of the Spectral Lines of Calcium	Yu. I. Ostrovskii and N. P. Penkin	219 (429)
Interferometric Method for the Determination of the Gas Density and Electron Concentration in Plasma	A. M. Shukhtin	222 (436)
Wave Functions of Diatomic Molecules with Strong Spin-Orbit Coupling	E. E. Nikitin	227 (443)
Influence of the Rotational Structure of Molecular Bands on Light Absorption by Layers of Finite Thickness	V. N. Soshnikov	229 (448)
Vibrational Spectra of Aromatic Compounds X. Calculation and Interpretation of the Vibrational Spectra of Pyridine and the Deuteriopyridines, Nonplanar Vibrations	M. A. Kovner, Yu. S. Korostelev, and V. I. Berezin	233 (457)
Influence of Solvent Viscosity on the Fluorescence Spectra of Certain Organic Compounds	A. S. Cherkasov and G. I. Dragneva	238 (466)
On Davydov Splitting and Polarization Ratio in the Region of the First Electronic Transition of Anthracene Crystal	M. S. Brodin and S. V. Marisova	242 (473)
Magnetic Rotation of the Plane of Polarization of Light in the Impurity Absorption Region	A. F. Lubchenko	244 (477)
Calculation of the Optical Properties of Small-Radius Electronic Centers in Ionic Crystals	I. V. Abarenkov, N. N. Kristofel' and M. I. Petrashen'	250 (487)
On the Theory of Thermal Ionization of F'-Centers	A. G. Cheban	253 (493)
Details of the Mechanism of Phosphorescence Stimulated by Light from the F-Band Region	I. A. Parfianovich and E. I. Shuraleva	257 (500)
Dependence of Yield and Other Optical Properties of Zinc Sulfide Phosphors on the Size of Uncrushed Crystals	V. L. Levshin and B. D. Ryzhikov	259 (505)
Measurement of the Transmittance of a Light-Scattering Medium as a Method of Studying Inhomogeneities in It	A. I. Slutsker and V. A. Marikhin	263 (512)
Increase of Precision in Isotopic Spectral Analysis	M. S. Kashtan and T. N. Khlopina	266 (518)
On a Possible Cause of the "Carrier" Effect in Spectral Analysis	Ya. D. Raikhsbaum and V. D. Malykh	269 (524)
An Integrating Sphere Attachment to the SF-4 Spectrophotometer for Measurement of Diffuse Reflection and Transmission Coefficients	A. S. Toporets	272 (528)

SHORT COMMUNICATIONS

A Method of Determining Separately the Coefficients of Absorption and Scattering in Turbid Media ..	V. A. Timofeeva	275 (533)
On the Influence of Vibrations on the Limiting Polarization of the Luminescence of Complex Molecules	S. I. Kubarev	276 (535)
Absorption of Liquid Water in the Long-Wavelength Part of the Infrared Spectrum (42-2000 μ)	A. E. Stanevich and N. G. Yaroslavskii	278 (538)
Registration of Time-Resolved Contours of Spectral Lines by Means of an Electron-Optical Converter	I. F. Balashov, M. P. Vanyukov, V. R. Muratov, and E. V. Nilov	279 (540)
Photoelectric Spectropolarimeter	V. A. Kizel' and V. I. Permogorov	281 (541)
Effect of p-Toluidene and Potassium Iodide on the Fluorescence and Photooxidation of 9,10,-di-n-Propylanthracene	T. M. Vember and A. S. Cherkasov	282 (544)
Spectroscopic Determination of Ion Mobilities in Mixtures of Rare Gases	V. M. Zakharova and Yu. M. Kagan	284 (547)
Polarization of the Luminescence from Molecular Crystals under β -Ray Excitation	V. I. Gribkov, N. D. Zhevandrov, and Sh. D. Khan-Magometova	285 (549)

(Contents continued on inside back cover)